

**On mathematical modelling a solid-liquid zone  
in a two-phase monocomponent system and in  
binary alloy**

by

**L. RUBINSTEIN**

School of Applied Science  
and Technology

The Hebrew University of Jerusalem

Mathematical models are proposed for a description of the state of solid-liquid zones ("mushy regions") in a monocomponent thermally conductive medium and in binary alloys.

**Introduction**

In what follows we try to offer phenomenological models for a mathematical study of the creation and development of solid-liquid zones in the process of solidification of monocomponent metals and binary alloys. Formulations of these models are prefaced by critical remarks to the problem treatment existing in the relevant literature. These remarks motivate the approach to the problem consideration which follows.

The concept of a mushy region for a monocomponent thermally conductive medium is considered in §1. This consideration leads to introducing the "two-temperature model" of a mushy region in a monocomponent medium. This model is derived in §2. Generalizations of this model for cases of binary alloys capable of forming a eutectic mixture and a continuous set of solid solutions are respectively offered in §§3 and 4. The main point of these generalizations consists in distinguishing between the concentration of a solute in the bulk of the liquid phase within the mushy region and the equilibrium concentration at phase-interfaces within this region. Appendix 1 is devoted to the rough estimate of possible values of heat exchange coefficients entering the models under consideration. Appendix 2 contains some additional remarks to the treatment of §3. Collection of notations is presented at the end of the paper.

## 1. The concept of "mushy region" for a monocomponent thermally conductive medium

The concept of "mushy region" in a monocomponent thermally conductive medium has been introduced by Atthey [4] in connection with the consideration of the process of the change of phase of such a medium where sources and sinks of heat are continuously distributed.

Atthey considers the simplest case of a medium of a constant density unchanged in the process of melting or solidification, so that no convection is involved. The mushy region is there described as a region where the solid and liquid phases coexist at a constant temperature equal to that of fusion.

At the first step of his study Atthey formulates the problem as a classical Stefan one. Further, after introducing the local enthalpy, he reformulates it in terms of a weak-solution. At this stage the mushy region is described as a region where the local enthalpy function has values belonging to the interval bounded by enthalpies of a pure solid and a pure liquid phase being at the same melting temperature.

Numerical evaluations based on the use an explicit finite difference scheme, as it has been described by Kamenomostskaja [15], indicate, as it is asserted by the author, the existence of a mushy region. However no theoretical proof of the existence of such region has been offered.

Unfortunately the very concept of "mushy region" is introduced by Atthey without explanation of the sense implicated by the verb "coexist", which is a crucial point in the problem. Indeed, the concept of the coexistence may be understood in two different senses to which correspond two different mathematical models of "mushy region", namely

- A: a model of a heterogeneous medium, and
- B: a model of a fictitious homogeneous medium.

### A. THE HETEROGENEOUS MEDIUM MODEL

In what follows we consider a thermally conductive medium of a constant density, so that no convection is involved, and assume, for the sake of simplicity, that we deal with one-dimensional problems.

We must, first of all, emphasize that each study of the process of heat transfer, which is based on the solution of a boundary value problem posed for the Fourier equation, is a macroscopic one, independently of the approach used—whether classical or any generalized one (weak, for instance). This means that very particle of a heterogeneous medium under consideration is a priori considered as large enough to apply to it the macroscopic equation of heat transfer. Only this allows us to operate with the usual heat conduction equation without introducing a fictitious homogeneous medium by means of some averaging procedure. Such an emphasis is, in particular, necessary for understanding the real sense of the concept of "mushy region" as introduced in Atthey's paper. That concept may apparently be treated in the following manner:

Let  $G$  be a mushy region. Then, it consists of a subset  $G_s$  of open regions occupied by a solid phase, and of a subset  $G_f$  of those occupied by a liquid phase:

$$\bar{G} = \bar{G}_s \cup \bar{G}_f \quad (1)$$

Let

$$F = \bar{G}_s \cap \bar{G}_f$$

be the set of points belonging to the phase interfaces. Then the usual Stefan condition

$$\dot{s}(t) = k_s u_{sx} - k_f u_{fx}$$

must be valid at every point  $x = s(t)$  of  $F$ . Since, by assumption, the temperature in both phases belonging to the mushy region  $G$  is identically equal to that of fusion, the right hand side of (3) is identically equal to zero. Thus, the set  $F$  does not vary in time. This means that if  $G^* \subset \bar{G}^* \subset G$  is arbitrarily taken proper subregion of  $G$  then  $G^*$  does not vary in time, either. But this conclusion contradicts the assumption that the sources of heat are continuously distributed within  $G$ . This means that the heterogeneous model of a mushy region is incompatible with the classical Stefan's approach to the description of the temperature field within multiphase monocomponent media.

Assume now that we deal with a medium where the region  $G_s$  occupied by particles of a solid phase is surrounded by the regions  $G'_f$  and  $G''_f$  occupied by these of the liquid phase. Assume that the initial temperature in  $G_s$  is lower and within  $G'_f \cup G''_f$  is higher than that of melting. The sources of heat of a finite strength are distributed continuously within the region under consideration. Evidently a new phase boundary may appear or the existing phase boundary may disappear both simultaneously and nonsimultaneously and their number may be arbitrarily large depending on the character of heat sources and on the conditions on fixed boundaries. Let  $t_0 > 0$  be the first moment of the appearance of a new phase boundary or of the disappearance of an existing one. The temperature distribution and the location of phase boundaries may be determined in the interval  $(0, t_0)$  as a classical solution to an ordinary Stefan problem. Taking  $t_0$  for a new initial moment and reformulating the problem as a classical one, we may prolong the solution till the second moment of the appearance of new phase boundaries or disappearance of existing ones. This process of prolongation, including the process of reformulation of the problem, is quite compatible with the classical Stefan's approach. At the same time at every interval of its existence the classical solution of the problem coincides with the weak one\*). Due to the uniqueness of the weak solution, we conclude that at each time it coincides with the classical one, if the latter is constructed after a proper reformulation of the problem, necessary in view of the appearance of new interfaces, or disappearance of the existing ones. However, the classical solution does not exhibit the existence of a mushy region if the latter is defined as

\*) This is true provided that the classical solution does not exhibit the appearance of undercooled/overheated regions.

above. This means that the mushy region, defined as a region where the local enthalpy function belongs to the interval bounded by its values for the pure solid and the pure liquid phases cannot appear either.

It is to be emphasized that we do not intend to discuss there the question of the reality of the existence of mushy regions, but only to indicate the internal inconsistency of the Atthey's heterogeneous medium model and discuss the applicability of the classical Stefan's approach and its generalizations based on introducing a concept of weak solution for describing the phenomena of creation and development of mushy regions. In order to tackle the last question, we shall propose the following approach.

#### B: THE MODEL OF A FICTITIOUS HOMOGENEOUS MEDIUM

Let us outline a possible approach to describing the temperature field in a heterogeneous medium composed of particles of different phases distributed chaotically.

We assume that particles of different phases (or more accurately at least of two different phase) are present in a very large number within every physical element of volume, but that the characteristic size of these particles is large enough in order to make macroscopic equations of mass, momentum and heat transfer applicable for the description of processes evolving in every individual particle. In such a heterogeneous region every physical element of volume which is, in a natural way, identified with a mathematically infinitesimal volume, contains infinitely large number of surfaces of weak or strong discontinuities\*) of at least one of the fields under consideration, so that the usual description of these fields is, strictly speaking, impossible. Therefore the mathematical treatment of such heterogeneous medium is always based on the process of homogenization, consisting in introducing a fictitious homogeneous medium instead of the real heterogeneous one.

This fictitious homogeneous medium is obtained by means of averaging all the fields under consideration over the physical element of volume, or over the subset of its points belonging to the phase considered. The first method of averaging introduces such characteristics of the fictitious homogeneous medium as the volume concentration and specific surface of every phase as well as the average velocity of the phase motion per unit of volume of the heterogeneous medium. The second method of averaging introduces such characteristics as composition and density of every phase or hydrodynamic pressure within it.

These two methods of averaging are well known and broadly applied for description of mechanical or chemical isothermal processes evolving in porous media [9], [5], and even in homogeneous solutions, although in the latter case being formulated implicitly [14].

---

\*) Let  $f$  be a function continuous in both one-sided vicinities of a surface  $S$ , as well as along  $S$ , but has a jump when crossing it. Then  $S$  is called the surface of strong discontinuity of  $f$ . The surface of strong discontinuity of one of the derivatives of a continuous function  $f$  is called the surface of its weak discontinuity.

Usually, the averaging of temperature is performed over the whole physical element of volume, and leads to the standard one-temperature description of the heterogeneous medium with chaotically distributed particles of different phases. Incomparably less known is the multi-temperature approach, based on the second method of averaging. This approach associates to every point of the fictitious homogeneous medium as many temperatures as many different phases are present in the physical element of volume under consideration [19], [20], [10].

Equations of heat transfer within a heterogeneous medium, which does not undergo the change of phase state, contain the heat exchange terms proportional to the difference of the temperature of different phases under consideration. The coefficients of the heat exchange entering such terms are proportional to the square of the specific surface of the interphase contact. This means that the difference between temperatures of different phases is very small. However the influence of the interphase heat exchange on the temperature distribution may be significant, and it is definitely so in cases where the process of the change of the phase state develops due to the influence of the conditions imposed on fixed boundaries, rather than by the impact of external sources or sinks of heat. However, in cases when there are continuously distributed sources (sinks) of heat of a relatively large strength, so that their impact on the temperature of both the phases is much greater than that of the interphase heat exchange, one may neglect the difference between averaged temperature of different phases within the same physical element of volume. Such a situation may be presupposed existing in the case which is considered in Atthey's paper. Thus, one may consider the problem of creation and development of a mushy region on the basis of the fictitious homogeneous model of a heterogeneous medium, but with the use of the usual one-temperature approach.

Let us recall that for the sake of simplicity, we restrict ourselves to considering the one-dimensional case where the mushy region is a single-connected one surrounded by regions entirely occupied by the solid and liquid phase, respectively. Assume that the mushy region is characterized by

$$s(t) < x < S(t) \quad (2)$$

and that the solid liquid phases are respectively located within the intervals  $0 < x < s(t)$  and  $S(t) < x < 1$ . Denote the temperature of the solid and of the liquid phase by  $u_s$  and  $u_f$ , and the concentration of the solid phase within the mushy region by  $\sigma$ . Let the melting temperature be equal to zero. Then, neglecting convection created by the motion of the free boundaries  $s(t)$  and  $S(t)$ , we find that

$$\begin{aligned} a_s^2 u_{sxx} + F_s(x, t) &= u_{st}; & 0 < x < s(t), & \quad t > 0, \\ a_f^2 u_{fxx} + F_f(x, t) &= u_{ft}; & S(t) < x < 1, & \quad t > 0. \end{aligned} \quad (3)$$

within the mushy region we evidently have

$$\gamma \dot{\sigma}(t) = -F(x, t) \quad (4)$$

where  $F$  is the power of the sources of heat located within that region and  $\gamma$  is the latent heat of fusion per unit of volume\*).

\*)  $F_f$  and  $F_s$  are proportional to  $F$ .

Stefan-like conditions on the free boundaries  $s(t)$  and  $S(t)$  take the form

$$\begin{aligned} k_s u_{sx} &= (1-\sigma) \gamma \dot{s} & \text{for } x=s(t) \\ -k_f u_{fx} &= (1-\sigma) \gamma \dot{S} & \text{for } x=S(t) \end{aligned} \quad (5)$$

and also

$$u_s=0 \quad \text{for } x=s(t); \quad u_f=0 \quad \text{for } x=S(t) \quad (6)$$

We must add there the requirements

$$u_s < 0 \quad \text{for } 0 < x < s(t); \quad u_f > 0 \quad \text{for } S(t) < x < 1, \quad (7)$$

and conditions on fixed boundaries  $x=0$  and  $x=1$ , as well as initial conditions

$$\begin{aligned} u_s(x, 0) &= h_s(x); & u_f(x, 0) &= h_f(x); & \sigma(x, 0) &= g(x) \\ s(0) &= s_0; & S(0) &= S_0 \end{aligned} \quad (8)$$

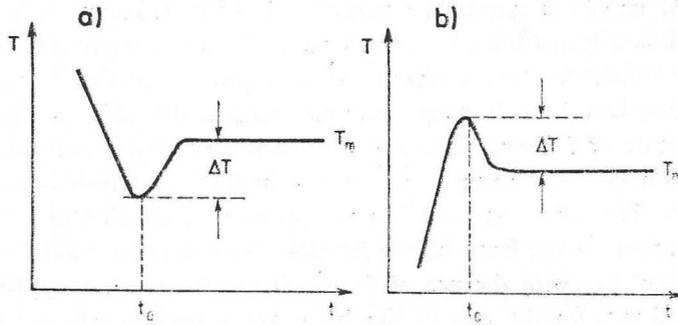


Fig. 1

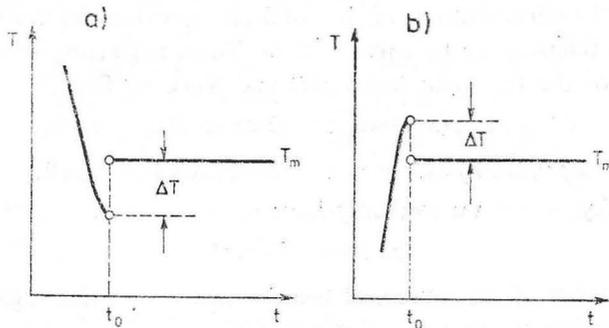


Fig. 2

There exists a serious difficulty in prescribing realistic values for  $s_0$ ,  $S_0$  and  $g(x)$ , when one considers the appearance of a mushy region in the course of the process evolution. Indeed, each process of the change of the phase state of the first kind, i.e. accompanied by the release or absorption of a latent heat, cannot evolve without some undercooling or overheating [13]. Typical graphs of temperature plot time have shapes shown in Fig. 1. The time  $\Delta t$  of exit from the undercooled (overheated) state is much shorter than the duration of the process of solidification (melting) of the undercooled (overheated) region. Therefore this exit may be considered as a spontaneous one, so that Fig. 1 may be replaced by Fig. 2. The depth  $\Delta T$  of undercooling (overheating) must be prescribed phenomenologically or, better, with a direct use of experimental data. In any case it cannot be evaluated in the course of solution of any Stefan-like problem.

As a first hypothesis, serving for determining the initial location of a mushy region, we propose to accept the following:

1. The mushy region at the moment of its creation may be described as a region where the spontaneous exit takes place from the undercooled (overheated) state.

2. At the moment of the spontaneous exit from this state the critical depth of undercooling (overheating) is reached at one point of that region.

Thus, the exit from the undercooled (overheated) state is assumed to be impossible if everywhere in the undercooled (overheated) region the temperature is more (less) than  $T_m - \Delta T$  ( $T_m + \Delta T$ ), and such an exit is unavoidable if the temperature is less or equal to  $T_m - \Delta T$  ( $T_m + \Delta T$ ) at least at one point of the region under consideration.

3. The solid (liquid) phase concentration in the mushy region is equal to zero at the first moment of its appearance, i.e. at the moment of a spontaneous exit of the system from the undercooled (overheated) state.

Whether this model is realistic must be clarified by the comparison of numerical evaluations with suitable experiments. In any case we believe that the critical remarks above may be useful for creation of a model of mushy region capable of withstanding comparison with experimental observations.

## 2. A mathematical model for a solid-liquid zone in mono-component medium

The problem of appearance and development of mushy region within mono-component media being under the action of continuously distributed sources (sinks) of heat is a special and rather artificially formulated version of a much more important problem of appearance and development of solid-liquid zones in course of solidification of monocomponent media.

The most important theoretically case is that where no distributed sources (sinks) of heat are within the medium under consideration. In such a case in contrast to the case of the existence of distributed sources of heat the one-temperature

approach above is not applicable for description of the solid-liquid zone development. Indeed, in such a case, the temperature within the solid-liquid zone would be identically equal to that of melting, so that the latent heat released in course of solidification cannot be utilized, or respectively, there is no source of heat to be absorbed by solid particles changing their phase state. Hence the mathematical model of the appearance of the solid-liquid zone and its development may be proposed only on the basis of a two-temperature approach.

However even after accepting such an approach a fundamental difficulty remains unsolved. There are two characteristics of a heterogeneous medium which determine its main physical properties: the concentration of phases and the specific surface of their interface. Equations determining the concentration redistribution and based on a phenomenological approach of fictitious homogeneous medium models must obviously contain terms dependent on that specific surface. Even as the growth of solid particles evolves preserving their geometrical similarity, the specific surface cannot be expressed in function of the phase concentration without prediction of the number of these particles as a function of time. Such a prediction cannot be done without a direct reference to concrete experimental data concerning, for example, the distribution of the stable centers of nucleation capable of growing into the solid particles of a macroscopic size. In what follows, we assume that one may use such an information. Hence the model which we are intending to propose is no more than a semi-empirical one.

Thus, let  $(x, y, z)$  be the Cartesian and  $(x, \varphi, \rho)$  the cylindrical coordinate system. Consider the cell

$$G = \{(\xi, \varphi, \rho) : x < \xi < x + dx; 0 < \varphi < 2\pi; 0 < \rho < R_0(\xi, \varphi)\} \quad (9)$$

so that

$$\int_0^{2\pi} d\varphi \int_0^{R_0(\xi, \varphi)} \rho d\rho = 4ab \quad (10)$$

and within it a body

$$G_s = \{(\xi, \varphi, \rho) : x < \xi < x + dx, 0 < \varphi < 2\pi; 0 < \rho < R(\xi, \varphi, t)\}. \quad (11)$$

Assuming that the solid-liquid zone has a periodic structure and that  $\delta G$  is a strip which is cut out from the element of periodicity of this structure, we refer to  $\delta G_s$  as a solid phase and  $\delta G_l = \delta G \setminus \delta G_s$  as a liquid. Let

$$\begin{aligned} \sigma &= \text{mes } \delta G_s \setminus \text{mes } \delta G = (4ab)^{-1} \int_0^{2\pi} d\varphi \int_0^{R(x, \varphi, t)} \rho d\rho \\ S &= (\text{mes } \delta G)^{-1} \int_0^{2\pi} d\varphi \int_x^{x+dx} R(1 + R_x^2)^{\frac{1}{2}} d\xi = (4ab)^{-1} \int_0^{2\pi} R(1 + R_x^2) d\varphi. \end{aligned} \quad (12)$$

We call  $\sigma$ —concentration of the solid phase, and

$S$ —specific surface of the solid-liquid phase interface.

In what follows we average functions of interest over  $G_f$ ,  $G_s$  and their boundaries. Everywhere we assume that the average of products may be replaced by the product of averages of all factors. This is admissible if the deviation of one of two factors from its average value is uniformly bounded, and the standard deviation of the second factor is small [20].

Integrating the equation of heat transfer

$$\operatorname{div} (k_f \operatorname{grad} \vartheta_f) = c_f \rho_f \vartheta_{ft} \tag{13}$$

over  $G_f$  we obtain

$$J = J^* \tag{14}$$

where

$$J dx = \int_{\partial(\delta G_f)} k_f \vartheta_{fn} d\sigma; \quad J^* dx = \int_{\delta G_f} c_f \rho_f \vartheta_{ft} d\omega, \tag{15}$$

we have

$$J dx = k_f \int_0^{2\pi} d\varphi \int_R^{R_0} \rho \vartheta_{fz} \Big|_{\xi=x+xd} d\rho - k_f \int_0^{2\pi} d\varphi \int_R^{R_0} \rho \vartheta_{fz} \Big|_{\xi=x} d\rho - k_f \int_x^{x+dx} d\xi \int_0^{2\pi} R (1 + R_x^2)^{\frac{1}{2}} \vartheta_{fn} d\varphi \tag{16}$$

where  $\underline{n}$  is a vector normal to  $\partial(\delta G_f)$  inward to  $\delta G_f$ . Thus

$$J = \left( k_f \left( \int_0^{2\pi} d\varphi \int_R^{R_0} \rho \vartheta_f d\rho \right)_x \right)_x + \left( k_f \int_0^{2\pi} R R_x \vartheta_m d\varphi \right)_x - k_f \int_0^{2\pi} R(x, \varphi, t) (1 + R_x^2(x, \varphi, t))^{\frac{1}{2}} \vartheta_{fn}(x, \varphi, R(x, \varphi, t)) d\varphi \tag{17}$$

where

$$\vartheta_f|_{\rho=R} = \vartheta_m \tag{18}$$

is the melting temperature.

Let

$$k_f \int_0^{2\pi} \vartheta_{fn} R (1 + R_x^2)^{\frac{1}{2}} d\varphi = J_n^f \int_0^{2\pi} R (1 + R_x^2)^{\frac{1}{2}} d\varphi = 4ab S J_n^f \tag{19}$$

where  $J_n^f$  is a flux of heat from the liquid phase into the solid one per unit of the phase-interface surface.

Define analogously the average temperature  $u_f$  by the equality

$$\int_0^{2\pi} d\varphi \int_R^{R_0} \rho \vartheta_f d\rho = u_f \int_0^{2\pi} d\varphi \int_R^{R_0} \rho d\rho = 4abu_f (1 - \sigma). \tag{20}$$

Then

$$J = 4ab \left( (k_f (u_f (1 - \sigma)))_x + \vartheta_m (k_f \sigma_x)_x - S J_n^f \right) \tag{21}$$

or, taking into account that  $\vartheta_m$  is a constant,

$$J = 4ab \left( (k_f (1 - \sigma) u_{fx})_x - (k_f (u_f - \vartheta_m) \sigma_x)_x - S J_n^f \right) \tag{21a}$$

Consider  $J^*$ . We have

$$J^* dx = c_f \rho_f \int_x^{x+dx} d\xi \int_0^{2\pi} d\varphi \int_R^{R_0} \xi \vartheta_{f_t} d\rho \quad (22)$$

Using definitions (12) we obtain

$$J^* = 4abc_f \rho_f ((1-\sigma) u_{f_t} - (u_f - \vartheta_m) \sigma_t). \quad (23)$$

Introducing (21) and (23) into (14) we obtain

$$(k_f (1-\sigma) u_{f_x})_x - (k_f (u_f - \vartheta_m) \sigma_x)_x - SJ_n^f = c_f \rho_f ((1-\sigma) u_{f_t} + (u_f - \vartheta_m) \sigma_t) \quad (24)$$

which may be rewritten in the divergent form:

$$\begin{aligned} \operatorname{div} (k_f (1-\sigma) \operatorname{grad} u_f) - \operatorname{div} (k_f (u_f - \vartheta_m) \operatorname{grad} \sigma) - SJ_n^f = \\ = c_f \rho_f ((1-\sigma) u_{f_t} + (u_f - \vartheta_m) \sigma_t) \end{aligned} \quad (25)$$

Quite analogously, considering heat transfer within  $\delta G_s$  we obtain

$$(k_s \sigma u_{s_x})_x + (k_s (u_s - \vartheta_m) \sigma_x)_x + SJ_n^s = c_s \rho_s (\sigma u_{s_t} + (u_s - \vartheta_m) \sigma_t) \quad (26)$$

or in the divergent form

$$\operatorname{div} (k_s \sigma \operatorname{grad} u_s) + \operatorname{div} (k_s (u_s - \vartheta_m) \operatorname{grad} \sigma) + SJ_n^s = c_s \rho_s (\sigma u_{s_t} + (u_s - \vartheta_m) \sigma_t) \quad (27)$$

Usual conditions of the dynamical compatibility (i.e. thermal Stefan conditions) may be written in the integral form

$$\gamma \rho_s \left( \int_x^{x+dx} d\xi \int_0^{2\pi} d\varphi \int_0^R (\xi, \varphi, t) \rho d\rho \right) = \int_x^{x+dx} d\xi \int_0^{2\pi} (k_s \vartheta_{sn} - k_f \vartheta_{fn}) R (1 + R\xi^2)^{\frac{1}{2}} d\varphi \quad (28)$$

which is equivalent to

$$\gamma \rho_s \sigma_t = S (J_n^s - J_n^f) \quad (29)$$

It remains to define fluxes  $J_n^s$  and  $J_n^f$ . We take

$$J_n^s = \alpha_s (\vartheta_m - u_s); \quad J_n^f = \alpha_f (u_f - \vartheta_m) \quad (30)$$

with coefficients of the heat exchange  $\alpha_s$  and  $\alpha_f$  which have to be determined experimentally or by the use of additional heuristic considerations. A possible version of determining coefficients  $\alpha_s$  and  $\alpha_f$  is offered in Appendix 1.

Now let us make the following remarks. Equations (24) and (26) are obtained for an element of the periodic structure, or more precisely for its cross-section by the strip  $x < \xi < x + dx$ . However, these equations include only such characteristics of the heterogeneous medium as concentration of one of the phases and its specific surface. At the same time, rewritten in the divergent form (25) and (27), these equations do not indicate anything on the orientation of that strip, i.e. of the cross-section where the temperature of a real heterogeneous medium is averaged. Therefore we consider the system (25), (27), (29), (30) as the system of equations describing

a three-dimensional homogeneous medium, modelling the process of development of a solid-liquid zone in a real monocomponent structure\*).

We have to add initial conditions, conditions on fixed boundaries and on interfaces: solid- (solid-liquid mixture) and liquid- (solid-liquid mixture). Concerning conditions determining the initial location and the size of the liquid-solid zone in the case of development of a solidification process of an initially homogeneous one-phase medium one may accept assumptions formulated in the first section. If, however, one begins with consideration of the system where the solid-liquid zone exists at the very initial moment, the temperature of both solid and liquid phases, as well as their concentrations must be prescribed.

Conditions on free boundaries  $S_s$  and  $S_f$  separating the solid-liquid zone from these of a pure solid and pure liquid ones must express the continuity of heat fluxes over those parts of  $S_s$  and  $S_f$  which intersect particles of the same phase in a real heterogeneous medium as well as the equality of the temperature to that of fusion. However, on those parts of  $S_s$  and  $S_f$  which intersect particles of different phases of a real heterogeneous medium the Stefan conditions must be imposed. Hence in a fictitious homogeneous medium boundary conditions on free boundaries are

$$\begin{aligned} u^s &= u_f = u_s = \vartheta_m \\ k^s u_n^s - k_s u_{sn} &= 0 & \text{on } S_s \\ k^s u_n^s - k_f u_{fn} &= \gamma \rho_s n_t \end{aligned} \quad (31)$$

and

$$\begin{aligned} u^f &= u_f = u_s = \vartheta_m \\ k_s u_n^s - k^f u_n^f &= \gamma \rho_s n_t & \text{on } S_f \\ k_f u_{nf} - k^f u_n^f &= 0 \end{aligned} \quad (32)$$

Here  $u^s$  and  $u^f$  are the temperatures respectively in the pure solid and pure liquid zones.

Besides these thermal conditions those determining the phase concentration on the free boundaries must be prescribed. In the case when the solid-liquid phase appears in the course of cooling of a homogeneous medium after the system has left its undercooled state, the most natural assumption is that of continuity of the solid phase concentration, which gives

$$\sigma|_{S_s} = \sigma_s = 1; \quad \sigma|_{S_f} = \sigma_f = 0 \quad (33)$$

Let us point out that  $k^s$  and  $k^f$  entering conditions (31) and (32) are physical coefficients of thermal conductivity of the medium under consideration in its solid and respectively liquid state. At the same time coefficients  $k_s$  and  $k_f$  entering equa-

\*) Actually, our choice of the method of derivation of equations (25), (27) has been motivated by its simplicity and clarity. Applying that technique of averaging which is described in Chap. II, paragraphs 1-3 of [20], one may derive these equations without use of the assumption that the solid-liquid zone has a periodic structure, and without a preliminary derivation of equations of a one-dimensional heat transfer.

tions (25), (27), (31) and (32) are no more effective parameters, dependent apparently on the phase connectedness, i.e. on the structure of the solid-liquid zone. It seems obvious that if both phases occupy connected region then one may suppose

$$k_s = k^s; \quad k_f = k^f. \quad (34)$$

On the other hand, it is sometimes accepted to define the coefficients of thermal conductivity of a porous medium by formulas similar to the Kirchhoff law for a system of electric conductors (18), namely

$$1/k_s = (1-\sigma)/k^f + \sigma/k^s; \quad 1/k_f = (1-\sigma)/k^s + \sigma/k^f. \quad (35)$$

Taking this into account, we accept as a working hypothesis equalities

$$\begin{aligned} k_s &= k^s k^f / (k^s (1-\beta_s) + k^f \beta_s) \\ k_f &= k^s k^f / (k^s (1-\beta_f) + k^f \beta_f) \end{aligned} \quad (36)$$

where coefficients  $\beta_s$  and  $\beta_f$  must depend on the structure of the zone so that\*

$$\beta_s = 1, \beta_f = 0 \text{ for } \sigma = 1; \quad \beta_s = 0, \beta_f = 1 \text{ for } \sigma = 0 \quad (37)$$

### 3. A mathematical model for a solid-liquid zone in a binary alloy capable of forming a eutectic mixture

We know only four papers where the problem of appearance and development of a solid-liquid zone in a binary alloy capable of forming eutectic mixture is treated mathematically, namely the papers by Tien and Geiger [23], Cho and Sunderland [8], Cannon and Alexiades [7] and Alexiades [3]. Of all these papers only that by Tien and Geiger contains formulation of the assumptions basic for the model under consideration as well as their motivation. Cho and Sunderland have only demonstrated that the problem formulated by Tien and Geiger may be solved in an analytically closed form being a self-similar one, but they do not discuss the essence of the model. Both Alexiades and Cannon [7] and Alexiades [3] refer in turn to the paper of Cho and Sunderland with the only aim of motivating their mathematical study but they do not consider the essence of the model, either. Thus, the only paper really offering a model to the process under study is that by Tien and Geiger.

Let us enumerate their basic assumptions.

1. The process of solidification is considered as a thermal one. The field of concentration within the liquid phase is not studied.

2. The solid-liquid zone is the only zone where the process of solidification evolves. This means that the only free boundaries entering the problem formulation are the interfaces: solid- (solid-liquid mixture) and (solid-liquid mixture)-liquid.

\*) Concerning the method of averaging, which leads to introducing the fictitious homogeneous multiphase medium, see also [5].

3. Concentration of solid particles within the solid-liquid zone varies linearly. It is equal to zero on the interface liquid- (solid-liquid mixture) and equal to the eutectic concentration of the more refractory component  $A$  of the alloy at points of the interface solid- (solid-liquid mixture).

4. The temperature of the free boundaries are those of "solidus" and "liquidus", and are taken as constants.

Other assumptions concretize the problem and have a technical rather than principal significance.

Let us try to decipher the real sense of these assumptions. The authors of [23] have not made any statements concerning the mass transfer conditions. Therefore one may only guess what a real process is under study there. Apparently one must presuppose that Tien and Geiger's model does not contradict the main postulate of the thermodynamics of irreversible processes according to which the state of local thermodynamic equilibrium holds at every point of the system. If so, then the concentration of a more refractory component of the alloy in its liquid phase, being in a contact with solid particles, must be equal to the equilibrium concentration defined by the diagram of the phase equilibrium. Since at the same time every point of the solid-liquid zone is considered in [23] as a point where the state of phase change takes place, we must conclude that the concentration within the bulk of the liquid phase is equal to the equilibrium concentration at every point of the solid-liquid zone. Moreover, since Tien and Geiger consider the problem as a thermal one, and do not consider the diffusion or the convective mass redistribution, their main assumption may only be understood as the assumption that the heat transfer, but not the mass transfer, determines the physical state of the system at every moment of the process evolution. However, this assumption contradicts the leading principle of chemical kinetics, according to which the evolution of the process is mainly determined by the slowest subprocess involved [12]. Apparently, coefficients of the thermal diffusivity in melted salts, for instance, are of order  $10^{-2}$  cm<sup>2</sup>/sec., while those of diffusion are of order  $10^{-5}$  cm<sup>2</sup>/sec. [6] For metals the first one is of order 1. Thus, the thermal diffusivity coefficients are more than  $10^3$  times larger than those of diffusion\*). Hence the slowest subprocess involved into the whole process of the heat and mass transfer within the mushy region is the mass transfer rather than the heat transfer. Thus Tien and Geiger actually have ignored the above mentioned principle of chemical kinetics.

In order to get an idea concerning the possible consequence of this neglect let us consider rather unrealistic case of a binary alloy, having infinitely large coefficients of diffusivity within both phases and the coefficient of diffusion equal to zero. For the sake of simplicity we equalize coefficients of thermal conductivity of the solid and liquid phases, so that in a steady state the temperature distribution is a linear one, and, following Tien and Geiger, assume that the concentration

---

\*) D. S. Wollkind and L. A. Segel [24] estimate the ratio of these coefficients as being of order  $10^6$ .

of the solute within the liquid phase of the mushy region coincides with the equilibrium value.

Assume that the alloy occupies the region  $0 < x < L$ , and that the temperature  $T$  at the ends  $x=0$  and  $x=L$  is respectively equal to  $T_0$  and  $T_1$ . Denote by  $\sigma$  the concentration of the solid particles in the solid-liquid zone, and by  $c$ —the fraction of a more refractory component  $A$  in the liquid phase. Let the equation of solidus be

$$(T - T_e)/(T_a - T_e) = (c - c_e)/(1 - c_e) \quad (38)$$

where the subscript  $e$  refers to the eutectic temperature and concentration, and  $T_a$  is a fusion temperature of pure  $A$ . Let the initial concentration  $c$  be equal to  $c_f$ , and the corresponding equilibrium temperature be  $T_f$ .

We assume that

$$T_0 < T_e < T_f; \quad 0 < c_e < c_f < 1. \quad (39)$$

Since the coefficients of diffusivity are assumed to be infinitely large, the steady state temperature distribution will be reached instantly. Let  $x_e$  and  $x_f$  be the boundaries of the solid-liquid zone. Then

$$T(x_e) = T_e; \quad T(x_f) = T_f, \quad (40)$$

and according to the assumption by Tien and Geiger

$$\sigma(x) = c_e(x_f - x)/(x_f - x_e); \quad (T - T_e)/(T_1 - T_e) = x/L. \quad (41)$$

Let  $\rho$  be the density of the component  $A$ . Then it follows from the definition of  $x_e$ ,  $x_f$ ,  $T(x)$  and  $c(x)$  that the mass of  $A$  within the region  $0 < x < x_f$  is equal to

$$M = \rho \left( x_e + \int_{x_e}^{x_f} (\sigma + (1 - \sigma)c) dx \right) \quad (42)$$

On the other hand the initial content of  $A$  in this region is

$$M_0 = c_f x_f, \quad (43)$$

and no material exchange is assumed to occur between the region  $(0, x_f)$  and the external region  $(x_f, L)$  since the coefficient of diffusion is equal to zero.

Computing integral (42) with the use of (38)–(41) one finds

$$(M - M_0)/M_0 = -(c_f - c^0) c_f^{-1} (1 - (T_e - T_0)(T_f - T_0)^{-1} (1 - c^0)(c_f - c^0)^{-1}) \quad (44)$$

where

$$c^0 = c_f + (1 - c_e)(c_e \tau/3 + \frac{1}{2}((c_e(1 - \tau) - \tau))), \quad c_f = c_e + (1 - c_e) \tau, \quad (45)$$

$$\tau = (T_f - T_e)/(T_a - T_e); \quad T_f = T_e + (T_a - T_e)(c_f - c_e)/(1 - c_e).$$

Let, for instance,

$$c_e = \frac{1}{2}; \quad \tau = \frac{1}{2} \quad (46)$$

then

$$(M - M_0)/M_0 = -(1 + 13(T_e - T_0)/(T_f - T_0))/36 \quad (47)$$

so that

$$0.03 < (M_0 - M)/M_0 < 0.39. \quad (48)$$

The equality (44) measures the degree of violation of the mass conservation law caused by the assumptions that a) the bulk concentration in the liquid phase and the temperature of both the phases are associated by the diagram of the thermodynamic phase equilibrium, and b) the coefficient of diffusion is equal to zero. Since the equality (44) characterizes the steady state only, it is independent of the assumption that the diffusivity coefficients are infinitely large.

It is quite obvious that in reality the mushy region does not exist in a steady state at all. Therefore one should consider a quasi-stationary state in which the distribution of temperature is close to the stationary one, but the concentration distribution corresponds to a relatively short duration of the process evolution. However, it can be shown that such a consideration cannot lead to any essential correction of the estimate (44), if the bulk concentration of the solute within the mushy region is equalized with the equilibrium one. A proof of this assertion is given in Appendix 2. The example considered there corresponds to a model in which coefficients of heat conduction, density and specific heat capacities have no jumps at the phase boundaries, and the specific latent heat of fusion is constant. However values of all these parameters are taken close to those for the alloy Pb-Bi. The value of  $(M_0 - M)/M_0$  calculated for this example is equal to 0.22 with  $M_0 = 37.5$  g. Correction due to the diffusion mass transfer up to the moment when the temperature distribution differs from the stationary one by 1% is equal to 0.1%. This demonstrates that, indeed, the correction due to diffusion into the mushy region from the pure liquid melt cannot change the above conclusion.

Let us point out that the assumption concerning the coincidence of the bulk temperature of both the phases and the bulk concentration within the liquid phase coincide with those connected by the diagram of the phase equilibrium is equivalent to the assumption that in the absence of any spatial gradients of concentration and temperature the phase change process evolves with infinitely large velocity, and just this assumption strongly violates the above mentioned basic principle of chemical kinetics.

Using Frank-Kamenetski terminology [12] one may say that the real process of creation and development of a solid-liquid zone in course of a binary alloy solidification evolves in the "exterior diffusion kinetic" region, what means that the limiting subprocess, determining the rate of the whole process of solidification is the process of the material exchange between the bulk of the liquid phase and the phase interfaces. In this sense the process under consideration is analogous to the process of absorption of a solute from solution saturating the external porous space of a porous absorbent. Therefore the phenomenological theory may be analogous to that underlying the theory of sorption-diffusion process. Such a theory, dealing with the exterior diffusion kinetics, has been proposed in papers by A. A. Zu-

chovitski et al [26], A. W. Tichonov et al [22], and Ja. L. Zabezinski et al [25], and has withstood the comparison with many experimental evidences. \*) Prior to formulating the model, we have to point out that, unlike to the case of a mono-component isobaric melt, we may now use the one-temperature approach. Indeed, in contrast to such a system the process of solidification of alloys is not an isothermal one. Hence, there is the heat flux along the solidifying melt, which means that there exists a receiver for the latent heat, released in course of the process evolution. However, the one-temperature approach does not allow to consider the limit case of alloy degenerated into a monocomponent melt. Taking this into account we introduce first a two-temperature model, and only after formulating it pass to its one-temperature simplification.

The model which follows is based on the same method of averaging which has been used in §2. \*\*) Let  $G_{s,f}$  be the solid-liquid zone,  $S_s$  and  $S_f$  be the free boundaries separating  $G_{s,f}$  appropriately from the pure solid and pure liquid zones  $G_s$  and  $G_f$ . Using the method based on replacing the real heterogeneous medium by the fictitious homogeneous one, we characterize the state of the system by:

$u^s$  and  $u^f$ —temperatures in  $G_s$  and  $G_f$ , respectively;

$v^f$ —the concentration of the more refractory component  $A$  of the binary alloy capable of forming a eutectic mixture in  $G_f$ ;

$v_f$ —concentration of  $A$  within the liquid phase of  $G_{s,f}$ ;

$u_s$  and  $u_f$ —temperatures of the solid and liquid phases in  $G_{s,f}$ ;

$u_m$  and  $v_m$ —average equilibrium temperature and concentration of  $A$  on the solid-liquid phase interfaces within  $G_{s,f}$ ;

$\sigma$ —concentration of the solid phase within  $G_{s,f}$ ;

$S$ —the specific surface of the solid phase within  $G_{s,f}$ .

Functions  $u_m$  and  $v_m$  are associated by the solidus equation

$$v_m = F(u_m). \quad (49)$$

Quite similarly to the equations of §2 we have

$$\begin{aligned} \operatorname{div}(k_f(1-\sigma)\operatorname{grad}u_f) - \operatorname{div}(k_f(u_f - u_m)\operatorname{grad}\sigma) - SJ_n^f &= \\ &= c_f \rho_f ((1-\sigma)u_{f,t} + (u_f - u_m)\sigma_t); \\ \operatorname{div}(k_s\sigma\operatorname{grad}u_s) + \operatorname{div}(k_s(u_s - u_m)\operatorname{grad}\sigma) + SJ_n^s &= \\ &= c_s \rho_s (\sigma u_{s,t} + (u_s - u_m)\sigma_t); \\ \gamma \rho_s \sigma_t &= S(J_n^s - J_n^f); \\ J_n^s &= \alpha_s(u_m - u_s); \quad J_n^f = \alpha_f(u_f - u_m). \end{aligned} \quad (50)$$

\*) See also [21] and [17].

\*\*) In what follows, we neglect the dependence of the thermal conductivity, specific heat capacity and density of the liquid phase upon its composition, the same concerns the specific latent heat. Taking into account the variation of the density and its jump on phase interfaces requires considering equations of motion of the particles of both phases. These equations coincide, in principle, with those of motion of every component of a heterogeneous system with particles of all phases distributed chaotically, which are derived in [20] under the assumption that the change of concentration of every phase is only the result of motion, but not of the process of the change of the phase state.

We must add equations of the mass transfer. Evidently

$$\operatorname{div} (D(1-\sigma) \operatorname{grad} v_f) - \operatorname{div} (D(v_f - F(u_m)) \operatorname{grad} \sigma) - SI_n = \\ = (1-\sigma)v_{ft} + (v_f - F(u_m))\sigma_t. \quad (51)$$

Here  $I_n$  is the flux of the component  $A$  from the bulk of the liquid phase to the phase interfaces within  $G_{sf}$ . Quite similarly to the thermal fluxes and to diffusion fluxes from the solution to the adsorbent in the Tichonov's theory [22] we take

$$(1-v_f)\sigma_t = SI_n; \quad I_n = \beta(v_f - F(u_m)). \quad (52)$$

Thermal conditions on free boundaries  $S_s$  and  $S_f$  coincide with those of §2, i.e.

$$u^s = u_f = u_s \triangleq u_m; \quad k^s u_n^s - k_s u_{sn} = 0; \quad k^s u_n^s - k_f u_{fn} = \gamma \rho_s n_t \text{ on } S_s \\ u^f = u_f = u_s \triangleq u_m; \quad k_s u_{sn} - k^f u_n^f = \gamma \rho_s n_t; \quad k_f u_{fn} - k^f u_{fn} = 0 \text{ on } S_f. \quad (53)$$

Further we must add there conditions of the dynamical compatibility for the mass transfer. They evidently are

$$v_f = F(u_m); \quad (1-\sigma)n_t = -Dv_{fn} \text{ on } S_s \\ v_f = F(u_m); \quad v_{fn} = v_f'' \text{ on } S_f. \quad (54)$$

Concerning the boundary conditions determining the solid phase concentration  $\sigma$  one may accept those by Tien and Geiger [23], i.e. to assume that

$$\sigma = 0 \text{ on } S_f; \quad \sigma = v_f \text{ on } S_s. \quad (55)$$

We do not formulate here the initial conditions and conditions on fixed boundaries. Concerning the initial conditions we may repeat what has been said in §2.

Finally we must emphasize again that we have no other way of determining the specific surface  $S$  than an empirical one. Now we may pass to the one-temperature simplification of the above model. Setting

$$k(\sigma) = k_s \sigma + k_f (1-\sigma); \quad c(\sigma) = c_s \rho_s \sigma + c_f \rho_f (1-\sigma) \quad (56)$$

and assuming that

$$u_s = u_f = u_m \triangleq u \quad (57)$$

we obtain, after adding equations (50) by sides,

$$\operatorname{div} (k(\sigma) \operatorname{grad} u) + \gamma \rho_s \sigma_t = c(\sigma) u_t \text{ in } G_{sf} \quad (58)$$

Analogously, conditions (53) turn into

$$u^s = u; \quad \gamma \rho_s n_t = k^s u_n^s - k u_n \text{ on } S_s \\ u = u^f; \quad \gamma \rho_s n_t = k u_n - k^f u_n^f \text{ on } S_f \quad (59)$$

Thus, equations of the one-temperature approach are (58), (51), (52), (54) and (59), to which the relevant initial conditions and those on the fixed boundaries as well as an empirical definition of the function  $S(\sigma, t)$  must be added.

#### 4. A solid-liquid zone in a binary alloy capable of forming a continuous set of solid solutions

We know only one paper devoted to mathematical modelling of the development of the solid-liquid zone in course of solidification of a binary alloy capable of forming a continuous set of solid solutions. This is the paper by M. K. Licht and S. B. Kuzminskaja [16]. Considering the one-dimensional process of solidification, they reduce the problem to that of determining the temperature of the system, the concentration of the solid phase and its specific surfaces. The authors of [16] write equations of diffusion within the solid and liquid phases of the solid-liquid zone, but assume at the same moment that the solute concentration at every point of that zone may be equalized with that of equilibrium, determined by equations of solidus and liquidus of the diagram of the phase equilibrium. After this the diffusion equation is used for determining the solid phase concentration.

As we have seen in §3 equalizing the solute concentration within the bulk of a liquid phase to the equilibrium value leads to an essential violation of the mass concentration law, even as the solute outflux (or, which is the same, the solvent influx) into the mushy region due to diffusion is taken into account. Therefore the critical remarks above concerning the Tien and Geiger's model remain valid with respect to that by Licht and Kuzminskaja, as well.

In what follows we write out equations of a model identical in its essence with that proposed above for alloys capable of forming a eutectic mixture. Equations of heat transfer within the solid and liquid phases of a mushy region i.e. equations (46) and (47) remain unchanged. Now let  $w_f$  and  $w_s$  be the concentrations of a solute respectively within the liquid and solid phase of a mushy region, whereas  $w^f$  and  $w^s$  be those in pure liquid and pure solid zones. Then instead of (51) we obtain

$$\begin{aligned} \operatorname{div} (D_f (1-\sigma) \operatorname{grad} w_f) + \operatorname{div} (D_f (\psi_f (u_m) - w_f) \operatorname{grad} \sigma) - S I_n^f = \\ = (1-\sigma) w_{ft} - (\psi_f (u_m) - w_f) \sigma_t. \end{aligned} \quad (60)$$

Analogously, within the solid phase of the mushy region

$$\begin{aligned} \operatorname{div} (D_s \sigma \operatorname{grad} w_s) + \operatorname{div} (D_s (w_s - \psi_s (u_m)) \operatorname{grad} \sigma) + S I_n^s = \\ = w_{st} + (w_s - \psi_s (u_m)) \sigma_t. \end{aligned} \quad (61)$$

Here

$$w_s = \psi_s (u_m), \quad w_f = \psi_f (u_m) \quad (62)$$

are equations of solidus and liquidus lines, and  $I_n^s, I_n^f$  are fluxes defined by

$$I_n^s = \alpha_s (\psi_s (u_m) - w_s); \quad I_n^f = \alpha_f (w_f - \psi_f (u_m)). \quad (63)$$

Equation (52) must now be replaced by

$$(w_s - w_f) \sigma_t = I_n^f - I_n^s. \quad (64)$$

Finally, the relevant boundary conditions become

$$\begin{cases} w^s = w_s = \psi_s(u_m), & w_f = \psi_f(u_m); \\ D^s w_n^s - D_s w_{sn} = 0; & (\psi_s(u_m) - \psi_f(u_m)) n_t = D_f w_{sn} - D^s w_n^s, \end{cases} \quad \text{on } S_s \quad (65)$$

$$\begin{cases} w^f = w_f = \psi_f(u_m); & w_s = \psi_s(u_m); \\ D^f w_n^f - D_f w_{fn} = 0; & (\psi_s(u_m) - \psi_f(u_m)) n_t = D^f w_n^f - D_s w_{sn}, \end{cases} \quad \text{on } S_f \quad (66)$$

and

$$\sigma = 0 \quad \text{on } S_f; \quad \sigma = \psi_s(u_m) \quad \text{on } S_s. \quad (67)$$

Naturally, the approximation

$$D^s = 0; \quad D_s = 0 \quad (68)$$

is admissible provided the process evolves under temperature not too high, otherwise the diffusion coefficients of solids could be quite large\*).

Equations of a one-temperature approximation may be obtained similarly to those in the case of the system capable of forming a eutectic mixture.

As everywhere above the specific surface, entering the equations, must be prescribed empirically.

## 5. Additional remarks

We have to emphasize again the character of the models derived above. Being phenomenological macroscopic models in their nature, they cannot give any description of such important process as, for example, dendrite growth. Such a theory may pretend to no more than predicting, by the use of certain experimental data, the rate of solidification, the size and location of mushy region, and the concentration of solid within it. However, one cannot expect obtaining any information concerning for example the crystallographic structure of mushy regions or any other properties dependent on the process evolution at the microscopic level.

We do not present there either results of numerical computations, or describe the possible numerical algorithm. We only point out here that in the case of creation and development of mushy region in a monocomponent medium the standard algorithms of discretization, proposed for the classical Stefan problem, are applicable (see, for example, [20 a]). One only has to use explicit finite difference approximations for computing  $\sigma$ , and the values  $(u_f - u_m)$  and  $(u_s - u_m)$ , entering equations (25) and (27). Values  $u_f$  and  $u_s$ , entering these equations (except for brackets above) may be computed by the use of implicit finite-difference approximations. The initial location of the mushy region will be determined from the numerical

\*) For example the coefficient of diffusion of Au in Pb at 285° is equal to  $4.6 \cdot 10^{-6}$  cm<sup>2</sup>/sec [11] what is only one order less than the characteristic values of the coefficients of diffusion for liquids.

solution of the standard Stefan-like problem (or even from one of heat conduction in a monophasic medium), including determining the moment  $t_0$  when the critical depth of undercooling is reached at least in one point of the region under consideration. By calculating the distribution of the temperature at  $t=t_0$ , we define the initial location of the mushy region. After this all computations will follow in a standard way.

In the case of solidification/melting of binary alloys similar ideas seem to be applicable. Since, however, one has to determine there the melting temperature at all time steps, the algorithm will include solution of some algebraic (generally speaking non linear) equations, what requires more careful consideration.

The pure mathematical problems of the existence, uniqueness and stability of the solution, as well as all numerical aspects, have to be subject of special studies.

#### APPENDIX 1. On the estimate of the coefficients of heat exchange

Coefficients  $\alpha_s$  and  $\alpha_r$  of heat exchange, entering equations (30) may be estimated in the following way.

Consider the problem

$$\begin{aligned} (a_s^2 u_{rr} + u_r/r) = u_t; \quad 0 < r < R = \text{const.} \quad (a_s^2 = k_s/c_s \rho_s) = \text{const.} \\ u_s(R, t) = \vartheta_m; \quad |u_s| < \infty; \quad u_s(r, 0) = f_s(r). \end{aligned} \quad (69)$$

Using Fourier expansion we obtain

$$u_s(r, t) = \vartheta_m + \sum_{n=1}^{\infty} \alpha_n \exp(-a_{sn}^2 t) J_0(\lambda_n r) \quad (70)$$

where  $\lambda_n$  is the  $n$ -th root of the Bessel function  $J_0(\lambda R)$  and  $a_{sn} = a_s \lambda$ ,  $\alpha_n$  are coefficients of Fourier-Bessel expansion of  $f(r) - \vartheta_m$ .

Expansion (70) gives

$$-k_s u_{sr}(R, t) = k_s \sum_{n=1}^{\infty} \lambda_n \alpha_n \exp(-a_{sn}^2 t (J_1(\lambda_n R))) = A, \quad (71)$$

On the other hand

$$2R^{-2} \int_0^R (u_s - \vartheta_m) r dr = 2 \sum_{n=1}^{\infty} R^{-1} \alpha_n \lambda_n^{-1} \exp(-a_{sn}^2 t) J_1(\lambda_n R) = B. \quad (72)$$

Using definitions (71) and (72) we obtain

$$\alpha_s = A/B \quad (73)$$

where  $A$  and  $B$  are defined by (71) and (72).

Considering the process in the stage of a regular regime, i.e. when the initial irregularities of the temperature distribution are eliminated, one may omit all terms of series entering (73) except for the first ones. This gives

$$\alpha_s = \frac{1}{2} k_s R \lambda_1^2 \quad (74)$$

It is known [1] that

$$\lambda_1 = 2.4/R \quad (75)$$

Thus

$$\alpha_s \cong 2.88k_s/R \cong 1.5k_s S/\sigma \quad (76)$$

since in the case under consideration (see definitions (12))

$$S = 2\pi R/4ab; \quad \sigma = \pi R^2/4ab \quad (77)$$

Now let us consider the problem

$$\begin{aligned} a_f^2 r^{-1} (ru_{fr})_r = u_{ft}; \quad R < r < R_0 \quad (a_f^2 = k_f/c_f \rho_f = \text{const}) \\ u_{fr} = 0 \text{ at } r = R_0; \quad u_f = \vartheta_m \text{ at } r = R; \quad u_f = f(r) \text{ at } t = 0 \end{aligned} \quad (78)$$

imitating the temperature distribution in a liquid particle. We have

$$u_f = \vartheta_m + \sum_{n=1}^{\infty} \beta_n \exp(-a_f^2 \mu_n^2 t) Z_0(\mu_n r) \quad (79)$$

where

$$Z_0(\mu_n r) = Y_0(\mu_n R) J_0(\mu_n r) - J_0(\mu_n R) Y_0(\mu_n r) \quad (80)$$

( $J_0$  and  $Y_0$  are Bessel and Neumann functions) and  $\mu_n$  is the  $n$ -th root of the equation

$$Z_1(\mu R_0) = 0 \quad (81)$$

Hence

$$\begin{aligned} k_f u_{fr}|_{r=R} &= - \sum_{n=1}^{\infty} \mu_n \beta_n \exp(-a_f^2 \mu_n^2 t) Z_1(\mu_n R) = A^*, \\ 2(R_0^2 - R^2)^{-1} \int_R^{R_0} r (u_f - \vartheta_m) dr &= \\ &= -2(R_0^2 - R^2)^{-1} \sum_{n=1}^{\infty} R \mu_n^{-1} \beta_n \exp(-a_f^2 \mu_n^2 t) Z_1(\mu_n R) = B^*. \end{aligned} \quad (82)$$

Hence in the regular regime

$$\alpha_f = A^*/B^* = \frac{1}{2}(R_0^2 - R^2) \mu_1^2 k_f/R. \quad (83)$$

In the case under consideration

$$(R/R_0) = \sqrt{\sigma}; \quad R = \sigma/2S. \quad (84)$$

At the same time approximately [2]

$$\mu_1 R \cong \pi (R_0/R - 1)^{-1}. \quad (85)$$

Therefore

$$\alpha_f = \pi^2 S^{-1} (1 + G^{1/2}) (1 - \sigma^{1/2})^{-1} k_f \quad (86)$$

Evidently these estimates of the possible values of the heat exchange coefficients are no more than heuristic ones.

## APPENDIX 2. Correction to the estimate (44)

As it has been said in §3, one has to introduce a correction to the estimate (44) on the mass deficit. We remind the reader that this estimate has been obtained in the framework of the Tien and Geiger's theory with applying the assumptions: 1) there is no mass transfer, so that the thermally stationary state of the system coincides with its true steady state, and 2) the bulk concentration of a solute within the liquid phase of the mushy region coincides with the equilibrium concentration.

Now we are going to introduce a correction to the estimate (44), taking into account the mass influx into the mushy region due to diffusion from the pure liquid zone within the time interval, when the stationary temperature distribution may be reached with a prescribed accuracy. In order to do this let us consider two problems, related to the thermics and the diffusion ones.

## A. The thermal problem

Assume that the whole latent heat  $q$  is released in the region  $(x_e, x_f)$  (i.e. in the mushy region defined in §3), so that

$$q = \gamma \rho \left( x_e + \int_{x_e}^{x_f} \sigma dx \right). \quad (97)$$

Assume further that this amount of heat is released by the instant source of heat located at the moment  $t=0$  in the point

$$x_0 = \frac{1}{2}(x_e + x_f). \quad (88)$$

Let  $\vartheta(x, t)$  be the temperature within the zone  $0 < x < L$  defined by the conditions

$$\vartheta(0, t) = T_0; \quad \vartheta(L, t) = T_1; \quad \vartheta(x, 0) = T_0; \quad 0 < x < L. \quad (89)$$

For the sake of simplicity, we shall assume that all the thermal parameters of both phases coincide and that the specific heat of fusion is a constant. Then, the stationary temperature  $T$  will coincide with that defined in §3, i.e.

$$T = T_0 + (T_1 - T_0) x/L. \quad (90)$$

Denote by  $\hat{T}$  its average value over the interval  $(x_e, x_f)$ , so that

$$\hat{T} = T_0 + (T_1 - T_0) (2L)^{-1} (x_e + x_f). \quad (91)$$

Let

$$\hat{\vartheta}(t) = (x_f - x_e)^{-1} \int_{x_e}^{x_f} \vartheta(x, t) dx \quad (92)$$

be the average temperature of this layer at the moment  $t$ . Define  $t_0$  by the condition

$$(\hat{\vartheta} - \hat{T})/\hat{T} \leq \beta \quad \text{for } t \geq t_0 \quad (93)$$

where  $\beta > 0$  is a prescribed number, and call  $\hat{\vartheta}(t_0)$  the quasistationary average temperature of the solid-liquid zone  $(x_e, x_f)$ , and  $t_0$ —the moment to which this quasistationary temperature can be reached.

We have

$$\vartheta(x, t) = T(x) + 2/L \sum_{n=1}^{\infty} \exp(-n^2 \pi^2 a^2 t/L^2) a_n \sin(n\pi x/L) \quad (94)$$

where  $a$  is the diffusivity coefficient and

$$\begin{aligned} a_n &= \int_0^L (q\delta(\xi - x_0) - (T_1 - T_0)\xi/L) \sin(n\pi\xi/L) d\xi = \\ &= q \sin(n\pi x_0/L) - (T_1 - T_0)(-1)^n/L. \end{aligned} \quad (95)$$

Hence

$$\begin{aligned} \hat{\Theta} &= \hat{T} + 2(x_f - x_e)^{-1} \sum_{n=1}^{\infty} a_n n^{-1} \exp(-n^2 \pi^2 a^2 t/L^2) \cos(n\pi x_e/L) - \\ &\quad - \cos(n\pi x_f/L). \end{aligned} \quad (96)$$

Assume that  $t_0 > 0$  is large enough. Then we may omit all terms of the series on the right hand side of (96) except for the first one.

Thus

$$\hat{\Theta}(t_0) - \hat{T} \cong 2(x_f - x_e)^{-1} \exp(-\pi^2 a^2 t_0/L^2) a_1 (\cos(\pi x_e/L) - \cos(\pi x_f/L)), \quad (97)$$

so that

$$t_0 \geq L^2 \pi^{-2} a^{-2} \ln(2\hat{T}a_1 \beta^{-1} (\cos(\pi x_e/L) - \cos(\pi x_f/L))). \quad (98)$$

### B. The diffusion problem

Assume that the whole mass deficit defined by the equality (44) is uniformly distributed at the initial moment  $t=0$  within the region  $(x_1, x_f)$ , and that the boundaries of the region  $(x_e, L)$  are impermeable. Then the diffusion redistribution of the mass deficit within the region  $(x_e, L)$  would be defined by the conditions

$$Dc_{yy} = c_t, \quad 0 < y < l = L - x_e,$$

$$c_y|_{y=0} = 0; \quad c_y|_{y=l} = 0; \quad c|_{t=0} = \begin{cases} 0 & \text{for } 0 < y < l_0 = x_f - x_e \\ c_0 = m/l_0 & \text{for } l_0 < y < l. \end{cases} \quad (99)$$

Here

$$m = M_0 - M \quad (100)$$

is the mass deficit defined by (44) and (43).

The part

$$\delta m = \int_0^{l_0} c(y, t_0) dy \quad (101)$$

of the whole mass  $m$  may be considered as the correction to the mass deficit, found in §3 by means of consideration of the stationary state.

We have

$$c(y, t) = c_0 \int_{t_0}^t g(y, \eta, t) d\eta \quad (102)$$

where  $g$  is the Green function of the problem (99)

$$g = l^{-1} + 2l^{-1} \sum_{n=1}^{\infty} \exp(-n^2 \pi^2 l^{-2} Dt) \cos(n\pi y/l) \cos(n\pi \eta/l). \quad (103)$$

Hence

$$c(y, t) = c_0 (1 - l_0/l) + 2\pi^{-1} \sum_{n=1}^{\infty} n^{-1} \exp(-n^2 \pi^2 l^{-2} Dt) \cos(n\pi y/l) \sin(n\pi l_0/l) \quad (104)$$

so that

$$m = c_0 l_0 (1 - l_0/l) - 2c_0 \pi^{-2} \sum_{n=1}^{\infty} n^{-2} \sin^2(n\pi l_0/l) \exp(-n^2 \pi^2 l^{-2} Dt). \quad (105)$$

Consider an example. Let

$$\begin{aligned} a^2 &= 0.3 \text{ cm}^2/\text{s}; & \gamma &= 10 \text{ cal/g}; & D &= 0.310^{-4} \text{ cm}^2/\text{s}; \\ k &= 0.09 \text{ cal/cm.s.}^0 \text{ C}; & c &= 0.03 \text{ cal/g.}^0 \text{ C}; & \rho &= 10 \text{ g/cm}^3; \\ c_e &= 0.50; & c_f &= 0.75; & T_e &= 125^0 \text{ C}; & T_a &= 300^0 \text{ C}; \\ & & & & T_1 &= 400^0 \text{ C}; & T_0 &= 25^0 \text{ C}. \end{aligned} \quad (106)$$

In this case

$$x_e = 2.67; \quad x_f = 5.00, \quad T_f = 212.5^0 \text{ C}, \quad (107)$$

and

$$M_0 = 37.5 \text{ g}; \quad (M_0 - M)/M_0 = 0.20; \quad q = 325 \text{ cal}. \quad (108)$$

Take

$$\beta = 0.01. \quad (109)$$

Then the quasistationary state may be reached to the moment  $t = 98.7$  s., so that we take

$$t_0 = 100 \text{ s}. \quad (110)$$

Then we find from (105) that

$$m = 0.0384 \text{ g}. \quad (111)$$

Hence

$$m/M_0 = 0.001. \quad (112)$$

Let us remind that in the example under consideration

$$(M_0 - M)/M_0 = 0.22. \quad (113)$$

Hence the correction due to diffusion into the mushy region from a pure liquid zone is negligible.

The data (106) are chosen close to those for Pb-Bi alloy. This means that one may consider results obtained as characteristic enough.

### Notations

$G$ —region.

$G_s$  ( $G_f$ )—subset of  $G$ , belonging to the pure solid (liquid) phase.

$G_{s,f}$ —subset of  $G$ —the mushy region.

$\cup$  and  $\cap$  are symbols of the operations of taking sum and crossection of sets.

$\bar{D}$ —closure of the set  $D$ .

Superscripts  $s$  and  $f$  refer to values defined in  $G_s$  and  $G_f$ , respectively.

Subscripts  $s$  and  $f$  refer to values defined in solid and liquid phases of the mushy region  $G_{s,f}$ .

Subscript  $m$  refers to values at phase interfaces.

$u$  (with an appropriate sub- or superscript)—temperature

$v, w$  ( —, —, —, —, —, —) — concentrations of the more refractory component  $A$  of alloy  $A : B$ .

$\sigma$ —concentration of the solid in mushy region.

$2a, 2b$ —periods in  $y$ - and  $z$ -directions of the periodic structure, considered in §2.

$k^s, k^f$ —physically defined coefficients of the thermal conductivity.

$k_s, k_f, k$ —effective coefficients of thermal conductivity in mushy region.

$c^s, c^f, c_s, c_f$ —specific heat capacities per unit mass.

$c$ —effective specific heat capacity within the mushy region in one-temperature models.

$\rho^s, \rho^f, \rho_s, \rho_f$ —densities.

$\rho$ —density (effective) of the mushy region in one-temperature models.

$a_s^2, a_f^2$ —coefficients of thermal diffusivity.

$\alpha, \beta$  (with an appropriate subscript) coefficients of the interphase heat and mass exchange per unit of the interface surface.

$S$ —specific surface of interfaces in the mushy region.

$\psi_s(u_m), \psi_f(u_m)$ —equilibrium concentrations of  $A$ , defined for solidus and liquidus lines.

Letters  $x$  and  $t$  used as subscripts denote derivatives with respect to  $x$  and  $t$ , respectively.

### References

- [1] ABRAMOWITZ M. and STEGUN I. A. (Eds) *Handbook of Math. Functions*. New York, Dover Publ., 1972.
- [2] Loc. cit. 1, 374.
- [3] ALEXIADES V. Three phase boundary problem in alloy solidification. Non-linear partial

- differential equations in engineering and applied sciences. R. L. Sternberg and A. J. Kalinowski (Eds). New York, M. Dekker, 1980, 101-109.
- [4] ATTHEY D. R. A finite-difference scheme for melting problems. *J. Inst. Maths and Applics*, **13** (1974), 353-366.
- [5] BEAR J. On the derivation of macroscopic description of transport phenomena in porous media by local volume averaging. Free Boundary Problems. E. Magenes (Ed). Proc. of a Seminar held in Pavia, September-October 1979, **1**, 9-30.
- [6] BRETSZNAJDER S. Properties of gases and liquids. Engineering methods of evaluations. Chemistry. M.-L. 1966 Transl. from Polish into Russian.
- [7] CANNON J. R. and ALEXIADES V. Free boundary problems in solidification of alloys. *SIAM J. Math. Anal.* **11** (1980), 254-264.
- [8] CHO S. H. and SUNDERLAND J. E. Heat conduction problems with melting and freezing. Trans. ASME, *J. Heat Transfer*. August 1969, 421-426.
- [9] DEVISON B. B. A motion of underground water. Several new problems of mechanics of continuous media. M.-L. Akad. Nauk 1939 (in Russian).
- [10] DREW D. A. and SEGEL L. A. Averaged Equations for two-phase flows. *Studies in Appl. Math.* **2** (1971), 265-231.
- [11] ФИЗИЧЕСКИЕ Энциклопедический Словар. М. Сов. Энциклопедия **1**, 1960.
- [12] FRANK-KAMENETSKI D. A. Diffusion and heat transfer in chemical kinetics. M.-L. Akad. Nauk SSSR 1947 (in Russian).
- [13] FRENKEL J. A. Kinetic theory of liquids. M.-L. AN SSSR 1945 (in Russian).
- [14] DE GROOT S. R. and MAZUR P. Non-equilibrium Thermodynamics. Amsterdam North-Holland 1962.
- [15] KAMENOMOSTSKAJA S. L. On Stefan Problem. *Mat. Sbornik* **53** (1961) 95, 489-514.
- [16] LICHT M. K. and KUZMINSKAJA S. B. On the solidification of binary alloys in an interval of temperatures. *Fizika Metallov i Metallovedenie*. **11** (1961) 6, 878-882 (in Russian).
- [17] POL'SKI B. and RUBINSTEIN L. On the dynamics of sorption from a solution with diffusion redistribution of solute concentration. *Latvian Mat. Ezegodnik*. **8** (1970), 193-204 (in Russian).
- [18] RUBINSTEIN L. Electrolysis in a dispersed system. *J. of the Chem. Soc.*, Faraday Trans. **11** (1977) 73, 528-544.
- [19] RUBINSTEIN L. I. On propagation of heat in heterogeneous media. *Izv. Akad. Nauk SSSR. Ser. Geogr. and Geophys.* **12** (1947) 1, 27-45 (in Russian).
- [20] RUBINSTEIN L. I. Temperature Fields in Oil Layers. *Nedra, M. Ch.* **2** (1972), 27-50 (in Russian).
- [21] TICHONOV A. N. and SAMARSKII A. A. Equations of Mathematical Physics. M., Fizmatgiz 1963, 163 (in Russian).
- [22] TICHONOV A. N., ZUCHOVITSKI A. A. and ZABEZINSKI Ja. L. Absorption of a gas from the air stream by the layer of a porous adsorbent. *J. Phys. Chem* **20** (1946), 113 (in Russian).
- [23] TIEN R. H. and GEIGER C. E. A heat transfer analysis of the solidification of a binary eutectic system. Trans. ASME, *J. Heat Transfer*. August 1967, 230-234.
- [24] WOLLKIND D. J. and SEGEL L. A. A nonlinear stability analysis of the freezing of a dilute binary alloy. *Phil. Trans.* **268 A** (1970), 351-380.
- [25] ZABEZINSKI Ja. L., TICHONOV A. N. and ZUCHOVITSKI A. A. Loc. cit. 22, *J. Phys. Chem.* **23** (1949), 192 (in Russian).
- [26] ZUCHOVITSKI A. A., TICHONOV A. N. and ZABEZINSKI Ja. L. Loc. cit. 22, *J. Phys. Chem.* **19** (1945), 253 (in Russian).
- [20a] RUBINSTEIN L. The Stefan Problem. *Math. Monograph Transl.* **27** (1971).

## Note

After this paper had been written we had the opportunity to read N. A. Avdonin's book: *Mathematical description of processes of crystallization*: 1980, Riga, Zinatne (in Russian). The content of the chapter 4 of that monograph is very close methodically to that of the §4 of our paper. However, there is a principal distinction. N. A. Avdonin puts the bulk concentration of the liquid phase within the mushy region equal to the equilibrium concentration on phase interfaces, what violates, as it has been explained in §3, the basic principle of chemical kinetics.

## Modelowanie matematyczne strefy przejściowej w pewnym dwufazowym układzie jednoskładnikowym oraz w stopie binarnym

Proponuje się modele matematyczne opisujące stan stref przejściowych („obszarów mieszaninych”) w jednoskładnikowym ośrodku przewodzącym ciepło oraz w stopach binarnych.

## О математическом моделировании твердо-жидкой зоны в некоторой однокомпонентной системе и в бинарном расплаве

Предлагается математические модели описывающие состояние твердо-жидких зон („переходных областей”) в однокомпонентной тепло-проводящей среде и в бинарных расплавах.

## The postscriptum

After the paper had been submitted to the journal, a number of new results became known to the author. These results must be mentioned and discussed in connection with the main text of the paper.

1. M. Shillor (1982) has considered the frontal motion of phase interfaces of each of two components, composing a heterogenous medium with chaotically distributed particles. His study was based on the use of the two-temperature model in its classical and weak formulations. Numerical computations, performed by him, have shown that the classical solution exhibits the appearance of an undercooled zone in a one-side vicinity of one of free boundaries, if the source term, describing the interphase exchange, is large enough. The weak solution exhibits the existence of a mushy region in this vicinity. These results are similar to those pointed out by N. Avdonin (1980) in connection with his study of the process of a directed crystallization.

2. In connection with these numerical results M. Shillor (1982) has proved that the classical solution of the problem, subject to Atthey's (1974) study, exhibits the generation of an overheated/undercooled zone at the time moment when the sources/sinks of heat become so great that their influence cannot be eliminated by

the efflux/influx of heat by means of thermal conductivity and by the absorption/release of the latent heat. At such a moment the existing free boundary changes the direction of its motion.

3. A. Meirmanov (1981) has indicated conditions of the generation of a mushy region in the weak solution of the Stefan problem for a nonhomogeneous Fourier equation, which coincide with those of the generation of an overheated/undercooled zone in a classical solution as indicated by M. Shillor (1982).

4. M. Primicerio (1981-1982) has constructed a "classical" model of generating the mushy region. His "classical" solution coincides with the respective weak solution. M. Primicerio, in his study, declines any discussion of the physical sense of the very concept of the mushy region referring only the reader to the shortened version of this paper (L. Rubinstein, 1982). His result is based, in its essence, on the use of the fundamental assumption that the local enthalpy may be a smooth function of time in the region remaining an isothermal one during a finite time period./ As far as it is known to me this assumption has been first used by Gelder and Gue (1975) and further by Crowley and Ockendon (1977). In all these papers, including that by M. Primicerio, this fundamental assumption was accepted as a not formulated postulat without any discussion. Probably this reflects introducing the local enthalpy as a principal unknown and the temperature as its function; this approach has become usual in papers dealing with weak solutions to the Stefan problem./

Considering all the above mentioned results one may see that there exists a serious inconsistency in papers dealing with classical and weak concepts of the solution of the Stefan problems. M. Primicerio's very important and mathematically complete study neither reduces nor explains the nature of this inconsistency namely because of a non-critical acceptance of the above-mentioned fundamental assumption.

In order to understand the source of this inconsistency one has to point out that a serious inaccuracy of the definition of the local enthalpy exists in all mathematical papers dealing with a weak solution of the Stefan problem beginning with that by Kamenomostskaja (1961) Indeed, in all these papers the following definition is used.

Let  $T$  be the temperature,  $s$  and  $f$  be subscripts referring to the solid and to the liquid states,  $T_m$  be the melting temperature. Then, assuming that specific heat  $c_s$  and  $c_f$  are constant as well as the specific latent heat  $\gamma$  (all per unit of volume) and that there is no jump of density, the local enthalpy is defined as

$$h(T) = \begin{cases} c_s T & \text{if } T < T_m \\ c_f T + \gamma & \text{if } T > T_m \end{cases} \quad (1)$$

whereas the accurate definition is

$$h(T) = \begin{cases} c_s T & \text{in the solid phase} \\ c_f T + \gamma & \text{in the liquid phase.} \end{cases} \quad (2)$$

Evidently the definition (1) excludes any possibility of considering the undercooled/overheated state of the material subject to the phase transform. From the other

hand the definition (2) allows us to deal with an overheated/undercooled state, which is quite compatible with the classical treatment of the melting/solidification problems in the presence of distributed sources/sinks of heat, but evidently cannot be used for introducing the concept of a weak solution.

From the other hand the enthalpy of a system of material particles, occupying a region  $D$ , so that its subsets  $D_{st}$  and  $D_{ft}$  belong at the time moment  $t$  to the solid and respectively to the liquid phase, is equal to

$$H(t) = \int_{D_{st}} c_s T d\omega + \int_{D_{ft}} (c_f T + \gamma) d\omega$$

and this function may be considered as a smooth function of time even when the temperature remains constant, if there exists transform of  $D_{st}$  into  $D_{ft}$  or inversely due to the action of distributed sources or sinks of heat. If, now,  $D$  is considered as a physical element of volume, identified with mathematically infinitesimal one, then the method of homogenization enters in force, the medium under consideration becomes not a real heterogeneous one but a fictitious homogenous medium, described by properties of two phases and their concentrations at every point of this medium. Under such an interpretation the local enthalpy  $h$  may become a smooth function of time even in isothermal conditions since in this case

$$h_t = -\gamma c_t$$

where  $c$  is the volume concentration of the solid phase.

This indicates the way for understanding the real sense of all papers dealing with the mushy regions on the basis of considering the weak solutions to the Stefan-like problems, including the above mentioned Primicerio's one.

However the principal question remains open. As it is emphasized in the main text of the paper the overheating/undercooling unavoidably precedes the melting/solidification if this process is accompanied with absorption/release of a latent heat. Theoretically the processes of melting and crystallization are symmetric /Frenkel, 1945/ but practically the overheating of solids is almost unobservable due to the greater instability of their overheated states. Therefore one may expect that predictions based on the weak solutions to the problem of the mushy region creation and development may be quite reasonable. However this is considerably less obvious when one deals with the process of solidification or recrystallization. In these cases the undercooling may be very deep and its duration may be very long. Therefore it is quite unclear whether predictions based on neglecting the unavoidable undercooling, i.e. based on the usual definition (1) of the local enthalpy, are reasonable ones. The answer may be obtained by means of a broad series of computations having their goal in the comparison of the temperature distribution predicted by a classical approach as it was done in the above mentioned M. Shillor's work and those based on considering the weak solutions to the problem.

We recall that our present work shows that the undercooled zone and respectively the mushy region appear at the same time and place. However the influence of input data on the duration of the overheated state/existence of the mushy region and their sizes remain unstudied.

## References

- [1] SHILLOR M.: A mathematical model for heat conduction or diffusion problems with phase transitions in heterogeneous media. Ph. D. Thesis, The Hebrew University of Jerusalem, 1982. [in preparation].
- [2] MEIRMANOV A.: An example of the nonexistence of the classical solution of the Stefan problem. *DAN SSSR*, **258** (1981) 547-549. [in Russian].
- [3] PRIMICERIO M.: Mushy regions in phase-change problems, to appear in: Proceedings of the Workshop on Applied Nonlinear Functional Analysis, Berlin, Sept. 7-12, Pitman. Preprint no 3 of the Università degli Studi di Firenze, Ist. Matematico U. Dini, 1981/1982.
- [4] GELDER D., GUY A. G.: Current problems in glass industry, in: Moving Boundary Problems in Heat Flow and Diffusion, J. R. Ockendon and W. R. Hodgkins, eds. Oxford 1975.
- [5] CROWLEY A. B., OCKENDON J. R.: A Stefan problem with a non monotone boundary. *J. Inst. Math. Appl.* **20** (1977), 269-281.
- [6] FRENKEL J. A.: Kinetic theory of liquids. AN SSSR, 1945. [in Russian].
- [7] AVDONIN N. A.: Mathematical description of the processes of crystallization. Zinatne, Riga 1980. [in Russian].
- [8] RUBINSTEIN L.: On the concept of mushy regions, in: Free Boundary Problems: Theory & Applications. Proc. of the Montecatini Symposium, A. Fasano and M. Primicerio, (Eds). Pitman, London 1982.