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INSTABILITY OF THE SELF-SIMILAR FRONT OF A PHASE TRANSITION

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UDC 536.42

The stability of self-similar diffusional processes with respect to small disturbances of plane, cylindrical, and spherical phase interfaces is investigated.

Self-similar processes of diffusion and heat conduction accompanying phase or chemical transformations are very common both in nature and in engineering. Many actual processes of vaporization, sublimation and condensation, dissolution, melting and crystallization, ablation, combustion, etc., enter precisely into self-similar asymptotic forms over a certain time interval dependent on the specifics of the initial conditions. In many cases, however, such an asymptotic stage of the process proves to be unstable, and the front of the phase interface or chemical reaction is considerably distorted. Two main forms of disruption of stability are possible in this case. Sometimes with weak "supercriticality," i.e., a small departure from the surface of neutral stability in parametric space in the region of instability, a regular periodic cellular structure appears at the front, the amplitude of which grows monotonically from zero with an increase in supercriticality. Sometimes upon a transition through the indicated surface disturbances of finite amplitude develop immediately at the front: dendrites appear which, losing stability in turn, form peculiar branched dendritic structures. Both these forms have been observed, e.g., in crystallization from melts and solutions [1]. A well-known example of the formation of dendrites is the appearance of hoarfrost or frost patterns on glasses upon the sudden cooling of air, when it becomes supersaturated with water vapor.

The questions of the conditions and the form of the disruption of stability are important in a scientific and an applied respect, since the onset of instability can radically alter

Ural State University, Sverdlovsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 40, No. 5, pp. 818-827, May, 1981. Original article submitted April 8, 1980.

0022-0841/81/4005-0497$07.50

both the character of the occurrence of the process and its result. For example, the structure of metal ingots obtained in the solidification of melts containing an admixture, and hence their strength and other physicomechanical characteristics, are largely determined by the properties of the dendrites which develop and the structure of the two-phase zone separating the crystals and melts, which depends on them [2]. Therefore, the problem of the stability of the front of a phase transition or chemical reaction with respect to small disturbances has been investigated repeatedly. In particular, it has been analyzed in application to the process of crystallization at plane [3], cylindrical [4], and spherical [5] surfaces.

However, the majority of the existing investigations in this direction contain a number of unjustified assumptions and inaccuracies. In [3-5], e.g., arbitrary assumptions are even made concerning the undisturbed concentration and temperature fields, the stability of which is essentially being investigated, while steady-state equations are mainly used for the description of small disturbances, which essentially depend on time by their very nature. At the same time, it is easy to show that the nonsteady terms, which are neglected in [3-5], have the same order of magnitude as the terms remaining in the equations.

In the present report this defect is eliminated and problems on the development of instability are analyzed within the framework of the general theory of hydrodynamic stability. In order not to encumber the main idea with superfluous calculations, we adopt certain simplifying assumptions which permit considerable abbreviation of the computations but do not affect the fundamental aspect of the matter. That is, we assume that the process (for determinacy we will consider the process of crystallization from a supersaturated solution) is self-similar, is limited to a single diffusional process, diffusion of the dissolved substance in the liquid phase, i.e., it occurs under isothermal conditions, and it does not lead to a change in specific volumes. We also neglect the dependence of the coefficient of diffusion on the concentration, assuming, for example, that the solution is dilute, and kinetic effects at the crystallization front, assuming that local thermodynamic equilibrium is achieved at it. We use the well-known solutions of the self-similar Stefan problem [6, 7] to describe the undisturbed processes with plane, axial, and spherical symmetries.

Plane Front

In this case the undisturbed process is described by the solution of the problem

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2}\,,\quad c \to c_\infty\,,\quad x \to \infty,$$
$$c = c_0\,,\quad (\rho - c_0)\,\frac{dX}{dt} = D\,\frac{\partial c}{\partial x}\,,\quad x = X(t), \tag{1}$$

with the last condition, reflecting the balance of the crystallizing substance at the crystallization front, serving as the definition of the quantity X(t). In the self-similar regime the concentration c depends on the single variable $x^\circ = x/X(t)$; the corresponding solution of (1) has the form

$$c = c_\infty - \Delta c\,\frac{\operatorname{erfc}(\alpha x^\circ)}{\operatorname{erfc}\alpha}\,,\quad \Delta c = c_\infty - c_0\,,$$
$$X(t) = (X_0^2 + 4\alpha^2 D t)^{1/2}, \tag{2}$$

while for the definition of the dimensionless coefficient α we have the equation

$$\alpha \exp(\alpha^2)\operatorname{erfc}\alpha = \frac{1}{\sqrt{\pi}}\,\frac{\Delta c}{\rho - c_0}\,. \tag{3}$$

From this it follows, in particular, that α is determined only by the values of the concentration in the crystal and in the solution near the crystal and far from it; usually $\alpha \ll 1$. At the crystallization front we have, from (2) and (3),

$$\frac{\partial c}{\partial x} = \frac{2\alpha^2(\rho - c_0)}{X}\,,\quad \frac{\partial^2 c}{\partial x^2} = -\frac{4\alpha^4(\rho - c_0)}{X^2}\,,\quad x = X(t). \tag{4}$$

For small disturbances imposed on the process (2) the problem is written in the form

$$\frac{\partial c'}{\partial t} = D\Delta c',\ c' \to 0,\ x \to \infty,$$

$$c' + \frac{\partial c}{\partial x}\, x' = -c_0 \Gamma K(x'),\ x = X(t), \tag{5}$$

$$(\rho - c_0)\frac{\partial x'}{\partial t} - \left(c' + \frac{\partial c}{\partial x}\, x'\right)\frac{dX}{dt} = D\left(\frac{\partial c'}{\partial x} + \frac{\partial^2 c}{\partial x^2}\, x'\right),\ x = X(t).$$

Here x' is the small disturbance in the shape of the front; K(x') is its curvature (positive when the front is concave in the direction of the solution); Γ is the effective coefficient of surface tension [3-5].

It is convenient to change to a coordinate system in which the front is stationary. Introducing the dimensionless variables

$$\varphi = \frac{c'}{\rho - c_0},\ \tau = \frac{u^2}{D}\, t,\ \xi = \frac{u}{D}\,[x - X(t)], \tag{6}$$

$$\begin{Bmatrix} \eta \\ \zeta \end{Bmatrix} = \frac{u}{D}\begin{Bmatrix} y \\ z \end{Bmatrix},\ \delta = \frac{u}{D}\, x',\ u = \frac{dX}{dt} = \frac{2\alpha^2 D}{X}$$

and allowing for (4), in place of (5) we obtain

$$\frac{\partial \varphi}{\partial \tau} - \frac{\partial \varphi}{\partial \xi} = \frac{\partial^2 \varphi}{\partial \xi^2} + \frac{\partial^2 \varphi}{\partial \eta^2} + \frac{\partial^2 \varphi}{\partial \zeta^2},\ \varphi \to 0,\ \xi \to \infty,$$

$$\varphi = -\delta - \gamma K(\delta),\ -\frac{\partial \varphi}{\partial \xi} = \frac{\partial \delta}{\partial \tau} + \delta + \gamma K(\delta),\ \xi = 0, \tag{7}$$

where K(δ) is understood as the dimensionless curvature in the variables (6) and we introduce the parameter

$$\gamma = \frac{c_0}{\rho - c_0}\,\frac{\Gamma u}{D}. \tag{8}$$

At large t the quantities u and γ can be treated approximately as constants, i.e., their weak time dependence can be neglected in the solution of (7). It is easy to see that this dependence shows up only in the extension of the resulting solutions to large time intervals $\Delta t \sim t$, in which there is no need to investigate the stability. An analogous simplification was adopted in [3-5].

We represent the functions φ and δ in the form

$$\begin{Bmatrix} \varphi \\ \delta \end{Bmatrix} = \begin{Bmatrix} \Phi(\xi) \\ \Delta \end{Bmatrix} \exp\left[\omega\tau + i(\varkappa_\eta \eta + \varkappa_\zeta \zeta)\right], \tag{9}$$

and, solving Eq. (7) with the boundary condition at infinity, we obtain

$$\Phi(\xi) = \Phi e^{-\lambda\xi},\ \lambda = (1/2)\{1 + [1 + 4(\omega + \varkappa^2)]^{1/2}\},\ \varkappa^2 = \varkappa_\eta^2 + \varkappa_\zeta^2. \tag{10}$$

Two conditions at the front from (7) yield a system of two homogeneous linear equations for the constants Φ and Δ; the characteristic equation of this system

$$(\lambda - 1)(1 - \gamma\varkappa^2) = \omega \tag{11}$$

defines ω as a function of the dimensionless wave number ϰ and the parameter γ. Disturbances for which ω > 0 are unstable.

We obtain the condition of instability for a disturbance with a given $\varkappa$ by using the definition of λ in (10):

$$\varkappa < 1/\sqrt{\gamma}. \tag{12}$$

Using the linear scale D/u introduced in (6) and the definition of γ, we rewrite this condition for the dimensionless wavelength of the disturbance:

$$\lambda > 2\pi \left(\frac{c_0}{\rho - c_0} \frac{\Gamma D}{u} \right)^{1/2}. \tag{13}$$

The increment of the growth of disturbances has the form

$$\omega = \frac{\gamma \varkappa^2}{2} (1 - \gamma \varkappa^2) \left[\left(1 + \frac{4}{\gamma^2 \varkappa^2} \right)^{1/2} - 1 \right] \tag{14}$$

and reaches a maximum at $\varkappa = \varkappa_m(\gamma)$; in the case of $\gamma \ll 1$, very important in practice, we approximately obtain

$$\varkappa_m \approx \frac{1}{\sqrt{3\gamma}}, \quad \lambda_m \approx 2\pi \left(3 \frac{c_0}{\rho - c_0} \frac{\Gamma D}{u} \right)^{1/2}. \tag{15}$$

In real systems the characteristic transverse size L of the front is limited; this means that there is a minimum attainable wave number $\varkappa_L \approx 2\pi D/uL$. Therefore, with an increase in γ to γ_L (i.e., for the given physical characteristics of the system, with an increase in the velocity of motion of the front to u_L) the instability ceases; for $\gamma \ll 1$ from (12) we have $\gamma_L \approx \varkappa_L^2$. In opposition to the conclusion drawn in [3], however, an idealized infinite front is unstable with respect to sufficiently long-wavelength disturbances, no matter how high the velocity u (or the parameter γ). The latter is connected with the fact that the single stabilizing factor, the presence of surface tension, acts very weakly on such disturbances. A model of such a type in [3], in which the quantity φ was treated as the solution of the steady-state Laplace equation corresponding to the nonsteady equation in (7), would correspond to a characteristic equation of the type of (11) in which λ would be calculated from (10) as before but with $\omega = 0$. It is clear that such a model leads to the former instability criterion (12) or (13), but Eqs. (14) and (15) are considerably altered.

Cylindrical Front

In this case the undisturbed self-similar process is described by the following equations, replacing (2):

$$c = c_\infty - \Delta c \frac{\mathrm{Ei}(-\alpha^2 r^{\circ 2})}{\mathrm{Ei}(-\alpha^2)}, \quad R(t) = (R_0^2 + 4\alpha^2 D t)^{1/2}, \tag{16}$$

$$r^\circ = r/R(t), \quad \Delta c = c_\infty - c_*, \quad c_* = c_0(1 + \Gamma/R).$$

(Here the influence of the surface effect on the equilibrium concentration of the substance in the solution near the front is allowed for.) For α we have, in place of (3),

$$-\alpha^2 \exp(\alpha^2)\, \mathrm{Ei}(-\alpha^2) = \Delta c/(\rho - c_*), \tag{17}$$

while the values of the derivatives at the front are

$$\frac{\partial c}{\partial r} = \frac{2\alpha^2 (\rho - c_*)}{R}, \qquad \frac{\partial^2 c}{\partial r^2} = -\frac{4\alpha^4 (\rho - c_*)}{R^2} \left(1 + \frac{1}{2\alpha^2} \right), \quad r = R. \tag{18}$$

In place of (7) we obtain, in dimensionless form,

$$\frac{\partial\varphi}{\partial\tau}=\frac{1}{\mu}\frac{\partial}{\partial\mu}\left(\mu\frac{\partial\varphi}{\partial\mu}\right)+\frac{\partial^2\varphi}{\partial\zeta^2}+\frac{1}{\mu^2}\frac{\partial^2\varphi}{\partial\theta^2},\quad \varphi\to 0,\ \mu\to\infty,$$

$$\varphi=-\delta-\gamma K(\delta),\quad \frac{\partial\varphi}{\partial\mu}=\frac{\partial\delta}{\partial\tau}+\left(1+\frac{1}{2\alpha^2}\right)\delta+\gamma K(\delta),\quad \mu=2\alpha^2, \tag{19}$$

where $K(\delta)$ is understood as the difference in the dimensionless curvatures of a slightly disturbed front ($r = R + r'$) and a cylinder ($r = R$), and we introduce the dimensionless quantities

$$\varphi=\frac{c'}{\rho-c_*},\quad \tau=\frac{u^2}{D}\,t,$$

$$\left\{\begin{matrix}\mu\\ \zeta\end{matrix}\right\}=\frac{u}{D}\left\{\begin{matrix}r\\ z\end{matrix}\right\},\quad \delta=\frac{u}{D}\,r',\quad u=\frac{2\alpha^2 D}{R}, \tag{20}$$

as well as the parameter (compare with (8))

$$\gamma=\frac{c_0}{\rho-c_*}\,\frac{\Gamma u}{D}. \tag{21}$$

Representing φ and δ in the form

$$\left\{\begin{matrix}\varphi\\ \delta\end{matrix}\right\}=\left\{\begin{matrix}\Phi(\mu)\\ \Delta\end{matrix}\right\}\exp\left[\omega\tau+i(\varkappa\zeta+n\theta)\right], \tag{22}$$

from (19) we find

$$\Phi(\mu)=\Phi K_n\left(\mu\sqrt{\omega^2+\varkappa^2}\right), \tag{23}$$

where $K_n(x)$ is a McDonald function, and the system of two linear equations for the constants Φ and Δ, the characteristic equation for which has the form (we use the well-known expression for the curvature of a slightly distorted cylindrical surface)

$$-\sqrt{\omega+\varkappa^2}\left.\frac{d\ln K_n(x)}{dx}\right|_{x=2\alpha^2\sqrt{\omega+\varkappa^2}}=\frac{\omega+1/2\,\alpha^2}{1-\gamma(n^2+\varkappa^2-1)}+1. \tag{24}$$

Let us make an approximate investigation of this equation for the case when $\alpha^2 << 1$, which offers the principal practical interest. We first assume that $\alpha^2\varkappa << 1$. Using the principal term of a series expansion of the McDonald function, near the curve of neutral stability, i.e., for $\alpha^2\sqrt{\omega} << 1$, from (24) with $n > 0$ we obtain

$$n\approx\frac{1+2\alpha^2\omega}{1-\gamma(n^2+\varkappa^2-1)},\quad \varkappa\ll\frac{1}{\alpha^2},\quad n>0. \tag{25}$$

Disturbances with wave numbers n and $\varkappa$ become unstable if

$$\gamma<\gamma_n^{(1)}(\varkappa)\approx\frac{n-1}{n}\,\frac{1}{n^2+\varkappa^2-1},\quad \varkappa\ll\frac{1}{\alpha^2},\quad n>0. \tag{26}$$

It turns out that when $n = 1$ disturbances are stable for any $\varkappa$ and γ, which is not surprising, since such disturbances correspond to a simple shift of the cylinder in a direction perpendicular to its generatrix. When $\gamma = \gamma_n^{(1)}(\varkappa)$ purely "longitudinal" disturbances ($\varkappa = 0$) with a given n first become unstable, while with a further decrease in γ ever more short-wavelength "transverse" disturbances are gradually excited and superimposed on them.

Equation (26) also determines the boundary of the instability region $0 < \varkappa < \varkappa(n)$ in the $(n, \varkappa)$ plane for a fixed γ. We have

$$\varkappa(n) \approx \left[\frac{1}{\gamma}\,\frac{n-1}{n} - (n^2-1)\right]^{1/2},\quad \varkappa \ll \frac{1}{\alpha^2},\quad n > 0. \tag{27}$$

For small enough γ this region first widens with an increase in n and then rapidly narrows. From the condition $\alpha^2 \varkappa << 1$ there follows the restriction $\gamma >> \alpha^4$ on the region of applicability of Eq. (27) for angular wave numbers n which are not too large.

For n = 0, which corresponds to axisymmetric disturbances, from (24) in the case of $\alpha^2 \varkappa << 1$ we obtain

$$\omega\left[\frac{1}{2\varkappa^2 \ln^2(\alpha^2\varkappa)} - \frac{2\alpha^2}{1-\gamma(\varkappa^2-1)}\right] \approx \frac{1}{1-\gamma(\varkappa^2-1)} + \frac{1}{\ln(\alpha^2\varkappa)}. \tag{28}$$

Such disturbances are unstable if the value of ω calculated from this is positive. It is easy to see that for any γ there is a region of long-wavelength unstable disturbances.

In the opposite limiting case of $\alpha^2 \varkappa >> 1$, using an asymptotic representation for the McDonald function, from (24) near the neutral stability curve we obtain

$$\sqrt{\omega+\varkappa^2} \approx \varkappa + \frac{\omega}{2\varkappa} \approx \frac{\omega + 1/2\,\alpha^2}{1-\gamma(n^2+\varkappa^2-1)} + 1,\quad \varkappa \gg \frac{1}{\alpha^2}, \tag{29}$$

in place of (25), from which it follows that in this case disturbances are unstable for which the parameters n and $\varkappa$ satisfy the inequality

$$\gamma < \gamma_n^{(2)}(\varkappa) \approx \left[1 - \frac{1}{2\alpha^2(\varkappa-1)}\right]\frac{1}{n^2+\varkappa^2-1},\quad \varkappa \gg \frac{1}{\alpha^2}. \tag{30}$$

Thus, when $\varkappa >> n$ the region of instability of short-wavelength transverse disturbances hardly depends on the presence of longitudinal disturbances. It is easy to see that estimates (26) and (30) coincide when $n >> 1$. Equations (29) and (30) are correct for any $n \geqslant 0$, while for small γ the condition $\alpha^2\varkappa >> 1$ is equivalent to the condition $\gamma << \alpha^4$.

From Eqs. (25) and (29) it is also easy to determine that in the case of $\gamma >> \alpha^4$ longitudinal disturbances with $n_m \sim 1/\sqrt{3\gamma}$ and $\varkappa_m \sim 0$ will have the maximum growth rate, while in the case of $\gamma << \alpha^4$ transverse disturbances with $n_m \sim 0$ and $\varkappa_m \sim 1/\sqrt{3\gamma}$ will have the maximum growth rate. For intermediate γ the fastest growing disturbances correspond to dimensionless wave numbers n_m and $\varkappa_m$ different from zero. In principle one can obtain representations of them by investigating Eq. (24) numerically. Here it is clear that $\lambda_m = 2\pi D/\varkappa_m u$ represents the characteristic scale of the cellular structure developing at the front or the characteristic distance between "nodes" along the cylinder from which the growing dendrites start. In the latter case the quantity n_m can be interpreted as the number of dendrites starting from one such node. If the very cylinder under consideration models a dendrite, developing at a plane crystallization front as a result of its instability, e.g., then λ_m and n_m characterize the distance between its primary branches and the number of branches at each node, respectively. (We note that in this discussion we entirely ignore the properties of symmetry of the crystal structure and the presence of preferred directions of crystal growth, so that its applicability is conditional in a certain respect [4].) The stability characteristics are affected, as is easy to see, by only two dimensionless parameters, α and γ; using their definition in (17) and (21), it is easy to clarify the dependence of these characteristics on the physical parameters and on the growth rate of the cylinder. In particular, it is seen that an increase in u promotes the contraction of the instability region and a decrease in λ_m, as occurred in the case of a plane front. In the self-similar problem under consideration the radius of the cylinder is not an independent parameter and affects the development of an instability only to the extent to which it determines the growth rate. Therefore, the assertion of the presence of a critical rate, upon exceeding which the given disturbances loses stability, primarily has physical meaning, but not a critical radius.

Spherical Front

In this case for the undisturbed self-similar process instead of (1) or (16), we obtain

$$c = c_\infty - \frac{\Delta c}{r^\circ}\,\frac{\operatorname{ierfc}(\alpha r^\circ)}{\operatorname{ierfc}\alpha},\quad R(t) = (R_0^2 + 4\alpha^2 Dt)^{1/2},$$
$$\operatorname{ierfc} z = \frac{1}{\sqrt{\pi}}\exp(-z^2) - z\operatorname{erfc} z,\quad \Delta c = c_\infty - c_*, \tag{31}$$
$$c_* = c_0\left(1 + \frac{2\Gamma}{R}\right),$$

instead of (3) or (17) the equation

$$2\alpha^2 \exp(\alpha^2)\operatorname{ierfc}\alpha = \frac{1}{\sqrt{\pi}}\,\frac{\Delta c}{\rho - c_*}, \tag{32}$$

and instead of (4) or (18) the equations

$$\frac{\partial c}{\partial r} = \frac{2\alpha^2(\rho - c_*)}{R},$$
$$\frac{\partial^2 c}{\partial r^2} = -\frac{4\alpha^4(\rho - c_*)}{R^2}\left(1 + \frac{1}{\alpha^2}\right),\quad r = R. \tag{33}$$

For small disturbances the problem is written in the form

$$\frac{\partial\varphi}{\partial\tau} = \frac{1}{\mu^2}\,\frac{\partial}{\partial\mu}\left(\mu^2\,\frac{\partial\varphi}{\partial\mu}\right) + \frac{1}{\mu^2\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\varphi}{\partial\theta}\right) + \frac{1}{\mu^2\sin^2\theta}\,\frac{\partial^2\varphi}{\partial\psi^2},$$
$$\varphi \to 0,\ \mu\to\infty;\ \varphi = -\delta - \gamma K(\delta),\ \mu = 2\alpha^2, \tag{34}$$
$$\frac{\partial\varphi}{\partial\mu} = \frac{\partial\delta}{\partial\tau} + \left(1 + \frac{1}{\alpha^2}\right)\delta + \gamma K(\delta),\ \mu = 2\alpha^2,$$

where $K(\delta)$ is the difference between the dimensionless curvatures of disturbed and undisturbed spheres, while the dimensionless quantities are defined in (20) and (21).

We write the quantities φ and δ in the form

$$\begin{Bmatrix}\varphi\\ \delta\end{Bmatrix} = \begin{Bmatrix}\Phi(\mu)\\ \Delta\end{Bmatrix} Y_n(\theta,\ \psi)\exp(\omega\tau), \tag{35}$$

with $Y_n(\theta, \psi)$ being spherical harmonics, while for $\Phi(\mu)$ we obtain from Eq. (34)

$$\Phi(\mu) = \frac{\Phi}{\sqrt{\mu}}\,K_{n+1/2}(\mu\sqrt{\omega}). \tag{36}$$

The characteristic equation of the system of linear equations for Φ and Δ, which follows from the last two equations in (34), has the form

$$-\sqrt{\omega}\,\frac{d}{dx}\left[\frac{1}{\sqrt{x}}\,K_{n+1/2}(x)\right]_{x=2\alpha^2\sqrt{\omega}} = \frac{\omega + 1/\alpha^2}{1 - \gamma(n-1)(n+2)} + 1. \tag{37}$$

Again taking $\alpha^2 \ll 1$, near the neutral stability curve we obtain

$$\frac{1}{2}(n+1) \approx \frac{\alpha^2\omega + 1}{1 - \gamma(n-1)(n+2)}. \tag{38}$$

It is easy to see that disturbances with n = 0 and n = 1, corresponding to a virtual spherically symmetric change in the radius of the sphere and its displacement in space, are stable and neutrally stable, respectively, for any value of γ. Disturbances characterized by a spherical harmonic with an index $n \geqslant 2$ become unstable if

$$\gamma < \gamma_n \approx \left(1 - \frac{2}{n+1}\right) \frac{1}{(n-1)(n+2)}. \tag{39}$$

Disturbances having a wave number

$$n_m \approx \frac{1}{3}\left[\left(4 + \frac{3}{\gamma}\right)^{1/2} - 2\right] \approx \frac{1}{\sqrt{3\gamma}} \tag{40}$$

grow faster than others. A comparison of Eqs. (37)-(40) with the analogous results in [5] indicates that, as in the cases of a plane and an axisymmetric front, the use of the models of [3-5], based on a number of approximations and intuitive assumptions, leads to considerable inaccuracies.

It follows formally from (39) that a growing sphere is stable with respect to small disturbances of all wavelengths if $\gamma > \gamma_2 \approx 1/12$, i.e., for

$$R \lesssim R^* = \frac{4 c_0 \Gamma}{\rho - c_0}(1 + 6\alpha^2) \tag{41}$$

(here we used the definitions of u, γ, and c_* given above). To describe the undisturbed concentration fields, however, we used self-similar equations which are approximately correct for $c_* \approx c_0 = \text{const}$, i.e., for diffusion toward the cylinder or sphere, only when $R \gg \Gamma$. This imposes a lower limit on the range of values of the radius R which it is admissible to analyze within the framework of the developed theory. In particular, it is seen from (41) that $\Gamma/R^* \sim 1$, i.e., the conclusion that there is a critical value of the radius such that smaller spheres are stable, like the same conclusion in [5], cannot be considered trustworthy. To verify it one must use other solutions of the Stefan problem, not self-similar, for unperturbed fields, the obtainment of which is a complicated independent problem.

In conclusion, we note that the generalization of the results obtained to more realistic situations, when the motion of the front of a phase transition or chemical reaction depends on several processes of diffusion or heat conduction and on kinetic phenomena at the front, only leads to complication of the calculations but does not present any fundamental new difficulties. The need to analyze such situations is determined not only by their applied significance, but also by the fact that many conclusions obtained earlier on the basis of models of the type presented in [3-5] must be reexamined.

NOTATION

c, weight concentration in solution; D, coefficient of diffusion; K, curvature; n, angular number; R, radius of cylinder or sphere; r, r', radial coordinate and disturbance of the surface r = R; t, time; u, velocity of front; x, y, z, linear coordinates; X, coordinate of front; x', disturbance of a plane front; α, parameter of growth rate; Γ, coefficient of surface tension; γ, parameter introduced in (8) or (21); δ, Δ, dimensionless disturbance of surface of the front and its amplitude; ξ, η, ζ, μ, dimensionless coordinates; θ, ψ, angular coordinates; $\varkappa$, dimensionless wave number; λ, wavelength of disturbance; ρ, concentration in solid; τ, dimensionless time; $\Phi(\mu)$, Φ, amplitudes of disturbances of concentration; dimensionless concentration; ω, dimensionless growth increment of disturbances. Indices: 0 and ∞ pertain to the states at a plane front and in the solution far from the front; an asterisk pertains to the state at a curved front; m pertains to the fastest growing disturbances; a degree sign pertains to self-similar variables.

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