Thermal instability of the phase-transition front in the decay of "frozen" metastable states

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It is shown that allowances for the finite rate of heat dissipation in the decay of "frozen" metastable states (FMS) leads to a thermal instability of the "explosive" type for the phase-transition front velocity. The critical parameters for the realization of this instability are calculated as functions of the heat-dissipation intensity and of the parameters that determine the thermal stability of the FMS.

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§1. INTRODUCTION

It is known that a supercooled state of the high-temperature phase can be obtained in a first-order phase transition. This metastable state is stable within certain limits, but sooner or later goes over into a phase that is stable at a given temperature T by formation and subsequent growth centers of this phase. The rates of these processes, and hence the rate of the relaxation of the metastable state, with the external conditions unchanged, are determined by the attained supercooling $\Delta T = T_t - T$, where T_t is the temperature of the phase transition between two equilibrium condensed phases of matter (for example, between a crystal and its melt or between two polymorphic or liquid-crystal modifications). It is important that the temperature dependence of the relaxation rate is qualitatively different in the case of small and large supercoolings.

If the supercooling is small ($\Delta T \ll T_t$) the relaxation rate (which is proportional to ΔT in first-order approximation) increases with decreasing temperature. In the other limiting case when the supercooling is large ($\Delta T \approx T_t$, i.e., $T \ll T_t$), the relaxation rate decreases with decreasing temperature because of the exponential decrease of the diffusion mobility of the atoms of the substance (in other words, because of the exponential increase in the viscosity of the metastable phase). We shall hereafter call this substantially supercooled state of the high-temperature phase a "frozen" metastable state (FMS).

A well known example of FMS are amorphous substances (glasses), which are "frozen" liquids. Other examples of FMS can be realized when various structural first-order transitions are frozen in the condensed state of matter. The best known methods of obtaining substances with FMS are fast cooling of the high-temperature phase (quenching) and various means of condensing substances on cold substrates.

The question of interest in this paper is the thermal stability of FMS, and it is therefore appropriate to emphasize some pertinent FMS features.

a) Strong disequilibrium in conjunction with a practically infinite lifetime at $T \ll T_t$. The former is connected with the freezing of the latent heat of the phase transition (in other words, the structural entropy of the high-temperature phase[1)]), and the latter with the activation character of the decay of the FMS (if u is the velocity of the phase-transition front, then $u \sim \exp(-E/T)$ at sufficiently low temperatures, where E is the activation energy.

b) Appreciable exothermy of the transition of the FMS into a stable phase (the transition heat Q is usually of the order of the latent heat ΔH of the phase transition).

c) In contrast to the case of small supercoolings ($\Delta T \ll T_t$), where the release of the transition heat hinders the relaxation into the stable phase, since $du/dT < 0$, the release of the transition heat in the decay of FMS ($T \ll T_t$) accelerates this process, since $du/dT > 0$ for FMS.

This positive feedback, with allowance for the activation character of the FMS decay, creates conditions for the appearance of thermal instability of the "explosive" type, when relatively small changes of a parameter can alter abruptly the FMS decay rate.

In this paper are considered in detail the conditions for the appearance of the indicated instability and its character, using as an example the motion of a plane front of a diffusionless phase transition in an FMS. Since the front velocity is determined by competition between the heat release on the front of the phase transition (PT) and the rate of heat dissipation, we consider first in Sec. 2 the pertinent self-consistent calculation, and introduce on its basis the concepts of fast and slow PT front propagation.

A successive analysis of the instabilities that set in is given in Sec. 3. In the concluding section are discussed briefly questions connected with organizing an experiment, and the conclusions are formulated.

§2. PT FRONT VELOCITY WITH ALLOWANCE FOR FINITE HEAT DISSIPATION

To solve the problems named in the heading of this section, it is necessary to specify a "bare" (nonrenormalized) kinetic relation $u(T_f)$ (T_f is the temperature of the PT front), and then, taking into account the finite rate of heat dissipation that leads to superheating of the front relative to the thermostat temperature T_0, calculate self-consistency the "renormalized" velocity $\tilde{u}(T_0)$ of the PT front as a function of T_0 (the tilde distinguishes the renormalized velocity from the unrenormalized velocity $u(T_0)$ at $T=T_f$).

We use below, for the sake of argument, the known[1] expression for the velocity of the front a diffusionless PT, produced by the normal growth mechanism[2)]:

$$u(T)=s\exp(-E/T)[\exp(-\Delta H/T_t)-\exp(-\Delta H/T)]. \quad (1)$$

Here s is a pre-exponential factor of the order of (and sometimes much less than) the speed of sound, E is the activation energy, and ΔH is the heat of the phase transition per particle at $T=T_t$. A schematic plot of $u(T)$ corresponding to (1) is shown in Fig. 1. Equation (1) is usually obtained[1] by calculating the resultant particle flux through a phase-separation boundary with an average potential relief of the type shown in the inset of Fig. 1. If $\Delta H\sim T_t$, it can be assumed in the region $T\ll T_t$, which corresponds to the FMS, that

$$u=u_0\exp(-E/T), \quad u_0\approx s\exp(-\Delta H/T_t). \quad (2)$$

We proceed now to take the heat dissipation into account. It can be shown that in the experimental case of real importance, that of thin layers (films) in the FMS, coated on substrates having high thermal conductivity, the heat-dissipation rate can be represented in the form $W=c(T-T_0)\tau_\theta$, where c is the specific heat of the substance, T_0 if the substrate temperature, and τ_θ is the time of thermal relaxation of the film. If d is the film thickness and α is the effective transparency of the film-substrate interface for phonons,[2] we have $\tau_\theta^{-1}=\alpha/dc$. The criterion for the applicability of such a description of the heat dissipation over the film thickness is satisfaction of the inequality $(d/l_\perp)^2\ll 1$, where $l_\perp$ is the thermal cooling length of the film ($l_\perp^2\equiv\varkappa\tau_\theta$, where $\varkappa$ is the thermal diffusivity of the film).

We consider now the propagation of a plane PT front with velocity u, choosing the z axis along the propagation direction and the x axis perpendicular to it (in the film plane). In a coordinate frame tied to the PT front, the heat-conduction equation is of the form

$$\frac{1}{\varkappa}\frac{\partial\theta}{\partial t}=\nabla^2\theta+\frac{1}{l_\parallel}\frac{\partial\theta}{\partial z}-\frac{\theta}{l_\perp^2}. \quad (3)$$

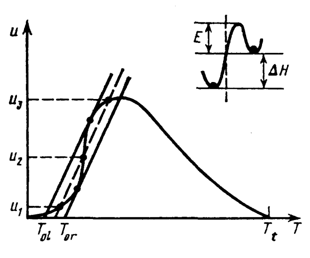

FIG. 1. Schematic plot of "unrenormalized" kinetic curve (bell-shaped). The three parallel inclined lines are the positions of the heat-dissipation curve for three substrate temperatures; u_1, u_2, and u_3 are the ordinates of the points of intersection with that head-dissipation curve for which $T_{0l}<T_0<T_{0r}$ (dashed line). Inset—averaged potential relief on the interphase boundary.

Here $\theta=T-T_0$ and $l_\parallel=\varkappa/u$. Equation (3) should be supplemented by the heat-balance condition on the PT front

$$Qu=\lambda'\frac{\partial\theta_f'}{\partial z}-\lambda\frac{\partial\theta_f}{\partial z} \quad (4)$$

and zero boundary conditions for the temperature and its gradient at $z=\pm\infty$, as well as by the condition that the temperature be continuous on the front, $\theta(0)=\theta'(0)$. Here λ is the thermal conductivity coefficient, and the primed quantities pertain to the stable phase.

In the one-dimensional case which is of interest to us so far, the solutions of (3) are simple in form

$$\theta(z)=\theta_f\exp(-\gamma z) \quad (z>0),$$
$$\theta'(z)=\theta_f\exp(\gamma' z) \quad (z<0), \quad (5)$$
$$\gamma=[(1+\nu^2)^{1/2}+1]/2l_\parallel, \quad \gamma'=[(1+\nu'^2)^{1/2}-1]/2l_\parallel'.$$

Here $\nu=v/u$, and the parameter v, which is essential in the analysis that follow and has the dimension of velocity, is connected with the previously introduced lengths by the relation $v/u=2l_\parallel/l_\perp$.

Substituting (5) in (4) we obtain another relation, on top of (1), between the temperature on the PT front and its velocity

$$2Q/\theta_f=c'[(1+\nu'^2)^{1/2}-1]+c[(1+\nu^2)^{1/2}-1]. \quad (6)$$

If we assume, to simplify the equations, that $c=c'$ and $\lambda=\lambda'$, Eq. (6) takes a particularly simple form

$$T_Q=\theta_f(1+\nu^2)^{1/2}. \quad (7)$$

Here θ_f has the physical meaning of the renormalization of the PT front temperature ($T_f=T_0+\theta_f$), and $T_Q=Q/c$ is, as follows from (7) as $\nu\to 0$, the maximum possible value of this renormalization, which is reached only for adiabatic motion of the PT front. On the other hand if $\nu\to\infty$, then $\theta_f\to 0$, corresponding to isothermal motion of the front. Figure 2 shows schematically the $u(T_f)$ dependence that follows from (7) for several values of $v=2(\varkappa/\tau_\theta)^{1/2}$. The smoother curves correspond to better heat dissipation (smaller values of τ_θ).

The foregoing treatment of θ_f enables us, given v and T_0 as functions of u, to introduce the important concepts of the rapid motion of the PT front [relatively poor heat dissipation, so that the renormalization of the front temperature and velocity is large, i.e., $\theta\gg T_0$, $\tilde{u}(T_0\gg u(T_0)]$, and of the slow regime [relatively good heat dissipation, small renormalizations, i.e., $\theta\lesssim T_0$, $\tilde{u}(T_0)\sim u(T_0)$]. It is precisely the possibility of realizing fast regimes at $T_0\ll T_t$ on account of "self-heating" of the PT front which is the characteristic feature of FMS.

If the PT front velocity is small enough so that the term $l_\parallel^{-1}\partial\theta/\partial z$ can be neglected in (3), this corresponds to the quasistationary description of the heat dissipation (the thermal field manages to "adjust itself" rapidly to the changes of u). Such an approximation calls formally for satisfaction of the inequality $l_\parallel\gg l_\perp$

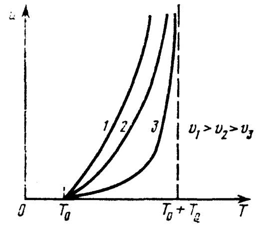

FIG. 2.

(or $\nu \gg 1$). If $v \gg u_m$, where u_m is the maximum velocity on the kinetic curve (see Fig. 1), then the corresponding "linearization" of the heat-dissipation curve, when (7) is transformed into

$$\theta_f = T_Q u/v, \tag{8}$$

is always justified (without, incidentally excluding the possibility of the regime in question being fast).

When the inverse inequality holds ($v \ll u_m$) fast regimes that are close to adiabatic ($\nu \ll 1$, $\theta_f \approx T_Q$) become possible, they can no longer be described in the quasistationary approximation, although the condition $v \ll u_m$ does not by itself exclude the possibility of the slow regimes with $\nu \gg 1$, which are describable by Eq. (8).

It is of interest to compare the characteristic dimensions of the temperature inhomogeneity due to heat dissipation on the PT front in the limiting cases $\nu \gg 1$ and $\nu \ll 1$. It is easy to show that in the former case $l \sim 2l_\perp$, whereas in the latter $l \sim l_\theta$ where $l_\theta \equiv u\tau_\theta$ is the distance traversed by the PT front during the time of the temperature relaxation. Since $v = 2l_\perp/\tau_\theta$, it follows that $l_\theta \sim l_\perp^2/l_\parallel \gg l_\perp$. Thus, on going from the slow regime to the faster one corresponding to smaller $l_\parallel = \varkappa/u$, the overheating of the front increases, and with it the characteristic thermal dimension l.

Returning now to the analysis of relations (1) and (7), we note that to find the $\tilde{u}(T_0)$ dependence which is of experimentally of interest, it suffices in principle to exclude T_f from relations (1) and (7) and solve the obtained equation with respect to u. However, in view of the nonlinearity of these relations and the associated possibility of ambiguity in $u(T_0)$ in the FMS region, it is convenient to perform the corresponding analysis graphically. To this end, one of the plots of Fig. 2, corresponding to the given value of v, must be superimposed on the kinetic curve (see Fig. 1) and, varying T_0, the ordinates of the points of intersection of these plots must be plotted against T_0. One of the possible results of such a plotting of $\tilde{u}(T_0)$ is shown in Fig. 3.

To assess the various qualitative possibilities that result from such a graphical analysis, we believe it is useful to simplify as much as possible the relations (1) and (7), expressing them in the forms (2) and (8). The analysis of (2) and (8), while retaining the main feature of the analysis of the initial equations (1) and (7), turns out to be much simpler, since it admits not only of a simple qualitative but also of a sufficiently accurate approximate analysis. To analyze Eqs. (2) and (8) it is convenient to change to a dimensionless velocity

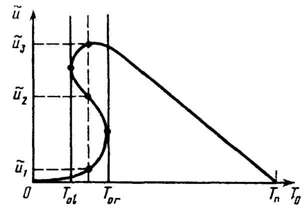

FIG. 3.

$w \equiv u/u_0$ and a dimensionless temperature $\tau \equiv T/E$. These equations take then the form

$$w = \xi(\tau - \tau_0), \tag{9}$$

$$w = \exp(-1/\tau), \tag{10}$$

where $\xi \equiv Ev/u_0 T_Q$. It is obvious from the forms of (9) and (10) that the character of the sought "nonrenormalized" $\tilde{w}(\tau_0)$ dependence is determined by the value of the only dimensionless parameter ξ, which has the meaning of the slope of the straightline (9).

A substantial role is played in the analysis by the quantity $\xi^* = 4/e^2$, which is equal to the slope of the tangent to the plot of $\exp(-1/\tau)$ at its inflection point (Fig. 4). It is obvious that if $\xi \geq \xi^*$, the sought $\tilde{w}(\tau_0)$ is single-valued for all τ_0. If, however, $\xi_0 < \xi < \xi^*$, where $\xi_0 = 1/e = e\xi^*/4$ is the slope of the line drawn from the origin and tangent to the plot of $\exp(-1/\tau)$ (see Fig. 4), the $\tilde{w}(\tau_0)$ plot assumes a characteristic s-shape (see Fig. 3). In this case, if $\tau_0 < \tau_{0l}$ or $\tau_0 > \tau_{0r}$, the function $\tilde{w}(\tau_0)$ is still single valued. If, however, $\tau_{0l} < \tau_0 < \tau_{0r}$, then each value of τ_0 corresponds to three values of $\tilde{w}$, only the largest and the smallest of which are stable, as will be shown in the next section. The corresponding relations, which make it possible to find the values of the critical temperatures τ_{0l} and τ_{0r} for a given ξ from the interval (ξ_0, ξ^*) can be obtained by noting that they are connected in simple fashion with the coordinates of the tangency points of the curves (9) and (10), designated hereafter τ_c ($c = r, l$). At these points not only expression (9) and (10), but also their derivatives are equal, from which we easily obtain a relation between τ_c and τ_{c0} in the form

$$\tau_c^2 - \tau_c + \tau_{c0} = 0. \tag{11}$$

The quantity τ_c is determined in turn from the equation

$$\eta_c^2 \exp(-\eta_c) = \xi, \tag{12}$$

where $\eta_c \equiv \tau_c^{-1}$.

The character of the solutions of the transcendental

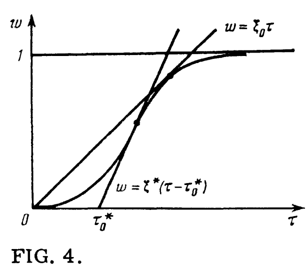

FIG. 4.

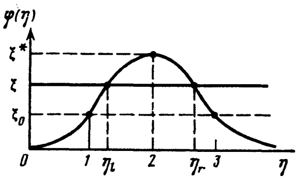

FIG. 5.

equation (12) can be easily represented by plotting its right and left-hand sides (Fig. 5). If $\varphi(\eta) \equiv \eta^2 \exp(-\eta)$, then it is easy to show that $\varphi(\eta)$ has a maximum at $\eta = 2$, with $\varphi(2) = \xi^*$. Therefore at $\xi > \xi^*$ Eq. (12) has no solution, in accord with the already noted single-valued character of the function $w(\tau_0)$ at $\xi > \xi^*$. On the other hand if $\xi < \xi^*$, Eq. (12) has two solutions, designated hereafter η_l and η_r. We note now that only those solutions of (12) for which $\eta \geq 1$ have physical meaning, since it is for them only that $\tau_{0c} \geq 0$ [see Eq. (11)]. Since $\eta_l \geq 1$ only if $\xi > \xi_0$, the function $\tilde{w}(\tau_0)$ at $\xi_0 < \xi < \xi^*$ has indeed the aforementioned s-shape [see curve 3 of Fig. 6, where the successive evolution of the plots of $\tilde{w}(\tau_0)$ can be traced as the parameter ξ is gradually decreased]. If $\xi = \xi_0$, then $\eta_l = 1$ and $\tau_{0l} = 0$ [See Eq. (11)], i.e. the "left-hand" interval where $\tilde{w}(\tau_0)$ is single valued vanishes completely (curve 4 of Fig. 6). Finally, if $0 < \xi < \xi_0$, the plot of $\tilde{w}(\tau_0)$ has a discontinuity at the origin (curves 5 and 6 of Fig. 6) and is single-valued only at $\tau_0 > \tau_{0r}$.

An essential feature of the considered non-single-valued $\tilde{w}(\tau_0)$ dependences is their "hysteresis" with respect to τ_0. Namely, if the representative point is initially on the lower branch and continues to remain on it as τ_0 increases up to τ_{0r}, the quantity $\tilde{w}$ must go over "jumpwise" (the dynamics of this transition is not considered in the present paper) at $\tau_0 > \tau_{0r}$ to the upper branch of the $\tilde{w}(\tau_0)$ curve. In analogy, if the representative point was initially on the upper branch, then a "drop" to the lower branch, i.e., a jumpwise decrease of the PT front velocity, must occur at $\tau < \tau_{0l}$.

We note, however, that for the $\tilde{w}(\tau_0)$ with the breaks (curves 5 and 6 of Fig. 6) motion along the upper branch is stable all the way to $\tau_0 = 0$, in contrast to the s-shaped plots (such as curve 3 of Fig. 6). In experiment this means that in an FMS with $\xi < \xi_0$ it is possible to excite a PT-front whose velocity remains finite even when the substrate is cooled to $\tau_0 = 0$.

Using (11), it is easy to calculate in terms of η_c the relative renormalization of the PT-front temperature

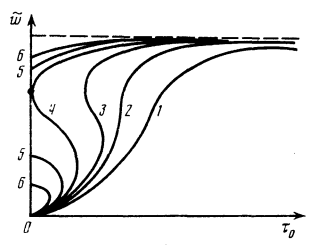

FIG. 6. Schematic plot of $\tilde{w}(\tau_0)$ for a number of values of the parameter ξ. 1) $\xi \to \infty$; 2) $\xi = \xi^*$; 3) $\xi_0 < \xi < \xi^*$; 4) $\xi = \xi_0$; 5, 6) $\xi > \xi_0$.

on account of the finite heat dissipation rate at the "breaks" points:

$$\chi_c \equiv \frac{\delta\tau_c}{\tau_{0c}} \equiv \frac{\tau_c - \tau_{0c}}{\tau_{0c}} = \frac{1}{\eta_c - 1} \quad (c = r, l). \tag{13}$$

The analogous renormalization of the velocity is found to equal

$$\frac{\delta w_c}{w_{0c}} \equiv \frac{w(\tau_c) - w(\tau_{0c})}{w(\tau_{0c})} = \exp(1 + \chi_c) - 1. \tag{14}$$

A curious feature of (13) is that $\chi_l \to \infty$ as $\eta_l \to 1$ (corresponding to $\xi \to \xi_0$), i.e., in this case the renormalizations indicated can be arbitrarily large for the upper branch. Expressions (13) and (14) are of interest also because they give the upper and lower limits of the renormalizations in "ordinary" (not critical) points for the lower and upper branches of the s-shape plot of $\tilde{w}(\tau_0)$, respectively.

To conclude this section, we note that if $\xi_0 < \xi < \xi^*$ the roots of (12) can be obtained with sufficient accuracy in explicit form if $\varphi(\eta)$ is approximated near $\eta = 2$ by its Taylor expansion

$$\varphi(\eta) = \xi^*[1 - (\eta - 2)^2/4]. \tag{15}$$

Then

$$\tilde{\eta}_c = 2[1 \pm (1 - \xi/\xi^*)^{1/2}]. \tag{16}$$

The accuracy of this approximation becomes worse as ξ decreases to ξ_0. Even at $\xi = \xi_0$, however, the error of η_c is of the order of 10%.

§3. INVESTIGATION OF STABILITY OF STATIONARY STATES OF PT MOTION IN FMS

The study of the stationary motion, considered in Sec. 2, of a plane PT front in an FMS has been actually reduced to an analysis of the self-consistent one-dimensional problem for the heat-conduction equation. Investigating its simplest variant [Eqs. (9) and (10)] we have shown that in the case of relatively poor heat dissipation the function $\tilde{w}(\tau_0)$ can turn out to be mutiply valued, and we have established a criterion for the onset of the corresponding thermal instability.

The critical temperature τ_{0r}, given by Eq. (12), at which this instability sets in has a physical meaning only if no morphological instability, i.e., instability to small bendings of the plane PT front, had set in earlier at $\tau_0 < \tau_{0r}$. It must be emphasized that in contrast to the similar investigations at small supercoolings ($\Delta T \ll T_t$) (which are considered in detail in Langer's review[3]), where the one-dimensional problem is usually stable because of the "negative feedback" mentioned in the Introduction, in the FMS case even the one-dimensional problem is generally speaking unstable. This distinguishes qualitatively the problem of thermal instability of a plane front of a PT in the FMS from the problem for the case of small supercooling. Therefore the question of the ratio of thresholds of the thermal instability in the one-dimensional problem to the morphological instability ($\partial/\partial x \neq 0$) is of considerable interest. The possibility of an oscillatory loss of stability is also of interest.

In the analysis that follows we shall not specify the form of the kinetic $u(T)$ relation. Assume that at a stationary unperturbed velocity u the PT front displacement comoving with the front in a coordinate frame due to fluctuations (of the velocity or of the form) u in the z direction is

$$z=\delta(t)e^{iqx}=\delta e^{-\Omega t}e^{iqx}\equiv\varphi(x,t), \tag{17}$$

where $\delta(t)$ is the amplitude of the perturbation ($\delta \to 0$) and q is the wave number. The system is stable relative to such a perturbation if the latter attenuates with time, i.e., $\dot{\delta}<0$ or in other words $-\Omega>0$ (or else, if complex frequencies are possible near the stability loss points, $\mathrm{Re}\,\Omega>0$). The PT front velocity change due to the perturbation (17) is

$$\delta u_\varphi=u_\varphi-u=\dot{z}=-\Omega\varphi. \tag{18}$$

On the other hand, δu_φ can be calculated with the aid of the kinetic equation (1) generalized to include the case of a curved interface in the form

$$u=s\exp(-\tilde{E}/T)[\exp(-\Delta\tilde{H}/T_t)-\exp(\Delta\tilde{H}/T)];$$

$$\tilde{E}=E-\alpha\omega K/2,\quad \Delta\tilde{H}=\Delta H+\alpha\omega K,$$

where α is the surface tension on the phase interface, ω is the specific volume, and K is the curvature of the interface. Then

$$\delta u_\varphi=\left(\frac{\partial u}{\partial K}\right)_T K_\varphi+\left(\frac{\partial u}{\partial T}\right)_K \delta T_\varphi, \tag{19}$$

where K_φ is the curvature of the perturbed surface $z=\varphi(x,t)$,

$$K_\varphi\approx z_{xx}''=-q^2\varphi, \tag{20}$$

and the correction to the front temperature is $\delta T_\varphi \equiv a\varphi$, where a is a still undetermined coefficient.

Perturbation of the boundary shape and of its velocity δu_φ leads to a corresponding change in the temperature field $T_\varphi \equiv T(z,x,t)$, so that

$$T_\varphi=T(z)+\delta T_\varphi(z,x,t),$$

where $T(z)$ is the unperturbed field determined in the preceding section [Eq. (5)]. The temperature field T_φ must be calculated self-consistently by starting from the complete heat-conduction equation (3), and must also satisfy relation (4) and the condition that the temperatures be equal on the true, i.e., unperturbed, phase separation boundary $z=\varphi(x,t)$.

Taking the smallness of δT_φ into account, we seek the solutions of (3) in the form

$$\theta(z,x,t)=\theta(z)+b\varphi\exp(-kz)\quad(z>0),$$
$$\theta'(z,x,t)=\theta'(z)+b'\varphi\exp(k'z)\quad(z<0), \tag{21}$$

where the still undetermined coefficients b and b' will eventually be expressed in terms of the previously introduced coefficient a, while the expressions for k and k' are

$$k=[(1+\nu^2+\varepsilon)^{1/2}+1]/2l_\parallel,\quad k'=[(1+\nu'^2+\varepsilon')^{1/2}-1]/2l_\parallel'; \tag{22}$$

$$\varepsilon=\varepsilon_q+\varepsilon_\Omega,\quad \varepsilon_q\equiv(2l_\parallel q)^2=\nu^2(ql_\perp)^2,\quad \varepsilon_\Omega\equiv-4l_\parallel^2\Omega/\varkappa=-\nu^2(\Omega\tau_\theta).$$

We now stipulate that $\theta|_\varphi=\theta'|_\varphi$. It is then easily shown that

$$b=a+\gamma\theta_f,\quad b'=a-\gamma'\theta_f, \tag{23}$$

where γ and γ' are given by Eqs. (5), and θ_f is the unperturbed renormalization of the PT front temperature.

Using now the balance equation (4) on the perturbed boundary $z=\varphi$, we get

$$-\Omega Q=\theta_f[\lambda'\gamma'^2-\lambda\gamma^2]+\lambda'k'b'+\lambda kb. \tag{24}$$

Substituting (23) in (24) and using (19), (20), and (24) we eliminate the quantity a and obtain finally

$$\Omega=\frac{q^2u_K'(\lambda'k'+\lambda k)+u_T'\theta_f[\lambda'\gamma'(\gamma'-k')-\lambda\gamma(\gamma-k)]}{(\lambda'k'+\lambda k)-Qu_T'}. \tag{25}$$

Equation (24) is the starting point for the analysis of the stability of a plane PT front to velocity perturbation of the type (17).

We investigate this expression below only for the simplest case when the thermophysical properties of both phases are equal. Thus, let $\lambda=\lambda'$ and $c=c'$.

We can then transform (25) into

$$\Omega=\left[q^2u_K'+\frac{\mu u}{2l_\parallel}\frac{(A+\varepsilon)^{1/2}-A^{1/2}}{(A(A+\varepsilon))^{1/2}}\right]\Big/\left(1-\frac{\mu}{(A+\varepsilon)^{1/2}}\right), \tag{26}$$

where we have introduced the dimensionless parameters A and μ defined by the relations

$$\mu\equiv\frac{Qu_T'l_\parallel}{\lambda}=\frac{u_T'}{u}T_Q,\quad A\equiv1+\nu^2. \tag{27}$$

Although this expression is convenient for the investigation of the instability of a plane front not only in the FMS region, we confine ourselves only to the latter, putting therefore $u_T'>0$, i.e., $\mu>0$. Notwithstanding these simplifications, the investigation of (26) is still quite cumbersome. We confine ourselves therefore to analysis of the limiting cases of physical interest, namely the thermal instability of stationary states of the one-dimensional problem considered in Sec. 2, and the morphological instability of an unstable plane PT front in a quasistationary approximation ($\nu\to\infty$).

a) We turn first to a consistent analysis of the thermal instability of the one-dimensional problem considered in the preceding section. It is important that we are able to analyze here the possible appearance of the vibrational instability typical of the upper branch of the function $\tilde{u}(T_0)$.

In this case $\partial/\partial x = 0$, so that we put in (26) $q = 0$ and $\varepsilon = \varepsilon_\Omega$. Assuming also $Z \equiv (A + \varepsilon_\Omega)^{1/2}$, it is convenient to rewrite (26) in the form

$$Z^2 - 2pZ + q = 0, \tag{28}$$

$$2p = \mu - A^{1/2}, \quad q = \mu(2-A)/A^{1/2}. \tag{29}$$

As already indicated in the beginning of this section, the motion of the PT front is stable if $\Omega > 0$ (or if $\mathrm{Re}\,\Omega > 0$). But from the definitions of Z and ε_Ω it follows that $\Omega\tau_0 = (A - Z_{1,2}^2)/\nu^2$. Then, if we put $\Phi_{1,2} \equiv A - Z_{1,2}^2$, the subsequent analysis of the thermal instability reduces to a determination of those values of the parameters μ and A at which $\Phi_{1,2} > 0$ if Φ is real, or $\mathrm{Re}\,\Phi_{1,2} > 0$ if Φ is complex. In the former case ($\Phi_{1,2} > 0$) we shall call the resultant regime statically stable, whereas in the latter case ($\mathrm{Re}\,\Phi_{1,2} > 0$, $\mathrm{Im}\,\Phi_{1,2} \neq 0$) it is vibrationally stable. Whether Φ is real or complex is determined in turn by the sign of the discriminant of the quadratic trinomial (28)

$$D = 4(p^2 - q) = \mu^2 + 2B\mu + A. \tag{30}$$

Where $B \equiv (A-4)\sqrt{A}$. Regarding (30) as a quadratic trinomial in μ and analyzing its discriminant $d \equiv 4(B^2 - A)$, it is easy to show that if $A > 2$ then $D > 0$ for all $\mu < 0$. But if $A < 2$ we have $D > 0$ only at $0 < \mu < \mu_1$ and $\mu > \mu_2$, whereas at $\mu_1 < \mu < \mu_2$ we get $D < 0$. Here μ_1 and μ_2 are given by

$$\mu_{1,2} = [(4-A) \mp (8(2-A))^{1/2}]/A^{1/2}. \tag{31}$$

It can also be shown that $\mu_1 \leqslant \mu_2$ always and that μ_1 increases monotonically and μ_2 decreases monotonically with increasing A (Fig. 7).

We consider now in succession the case of static instability. Besides the inequality $D > 0$, the region of permissible values of μ and A is determined then by simultaneous satisfaction of also the conditions $Z_{1,2} > 0$ and $\Phi_{1,2} > 0$. Omitting the straightforward but unwieldy analysis of the compatability of these two inequalities, we present only its results in the form of Table I. An omission in the table means that the inequality does not hold at any value of μ, and $\tilde{\mu}$, μ_0, and μ_k are defined by the relations

$$\tilde{\mu} = \sqrt{A}, \quad \mu_0 = A^{3/2}/(A-1), \quad \mu_k = 3\sqrt{A} = 3\tilde{\mu}. \tag{32}$$

Finally, allowance for the limitations imposed by the inequality $D > 0$ restricts even more the permissible

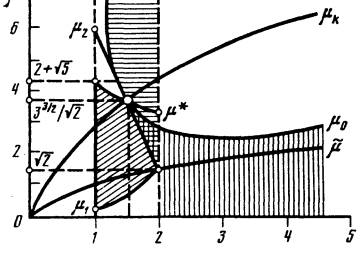

FIG. 7.

TABLE I.

A	μ	
	$\Phi_1>0$; $Z_1>0$	$\Phi_2>0$; $Z_2>0$
$1<A<3/2$	$\tilde{\mu}<\mu<\mu_k$	$\tilde{\mu}<\mu<\mu_k$; $\mu>\mu_0$
$3/2<A<2$	$\tilde{\mu}<\mu<\mu_0$	$\mu>\tilde{\mu}$
$A>2$	$\mu<\mu_0$	–

ranges of A and μ (Table II). It is convenient to plot the results on the (μ, A) plane (see Fig. 7). It shows plots of μ_1, μ_2, μ_0, $\tilde{\mu}$, and μ_k vs. A, and the two stability regions of the "statically stable" solutions are horizontally and vertically hatched. The stable solution is unique only for $A < 3/2$ ($\Phi_2 > 0$) and for $A > 2$ ($\Phi_1 > 0$). In the region $3/2 < A < 2$ there are at $\mu_2 < \mu < \mu_0$ two stable solutions corresponding physically to the s-shaped plot of $\tilde{u}(T_0)$ discussed in Sec. 2.

It is curious to note that the equation $\mu = \mu_0(A)$ for the boundaries of the instability regions (outside the interval $3/2 < A < 2$) coincides with the equation for the points of tangency of the $u(T)$ curve and the plot of the heat-dissipation equation (7) written in the form

$$u_T' = \frac{v}{T_Q}\left(1 + \frac{1}{\nu^2}\right)^{3/2}. \tag{33}$$

We consider now the possibility of realizing vibrationally unstable regimes corresponding to $\mathrm{Im}\,\Phi \neq 0$. We note *in passim* that these results could not be obtained in terms of the analysis of the stationary regimes in Sec. 2. The necessary condition for the onset of vibrationally stable regimes is satisfaction of the requirement $D < 0$. This immediately subjects the admissible parameters to the inequalities

$$1 < A < 2, \quad \mu_1 < \mu < \mu_2. \tag{34}$$

An additional limitation is also the requirement

$$\mathrm{Re}\,\Phi = A - (p^2 + D) > 0. \tag{35}$$

It follows from it that, besides (34), it is necessary to satisfy the inequality $\mu < \mu^*$, where

$$\mu^* = [2 + (4 + A^2)^{1/2}]/A^{1/2}. \tag{36}$$

It is easy to show that $\mu^*(A)$ is a monotonically decreasing function of A in the interval $1 < A < 2$ (see Fig. 7) and that $\mu^*(1) = 2 + \sqrt{5}$. With these remarks considered, the region of vibrationally stable states is defined by the relations

$$1 < A < 3/2, \quad \mu_1 < \mu < \mu^*, \qquad 3/2 < A < 2, \quad \mu_1 < \mu < \mu_2 \tag{37}$$

TABLE II.

A	μ	
	$\Phi_1>0$; $Z_1>0$; $D>0$	$\Phi_2>0$; $Z_2>0$; $D>0$
$1<A<3/2$	–	$\mu>\mu_0$
$3/2<A<2$	$\mu_2<\mu<\mu_0$	$\mu>\mu_2$
$A>2$	$\mu<\mu_0$	–

and is obliquely hatched in Fig. 7. We note now that on the lines $\mu=\mu^*(A)$ we have $\mathrm{Re}\,\Phi=0$. On the other hand, recognizing that

$$\mathrm{Im}\,\Phi=\pm 2p(|D|)^{1/2},$$

it is easy to show that $\mathrm{Im}\,\Phi(\mu^*)\sim 1$ as $A\to 1$. Thus, for states with $A\to 1$ and $\mu\to\mu^*(A)$ a situation arises wherein $\mathrm{Re}\,\Phi \ll \mathrm{Im}\,\Phi$, i.e., the velocity fluctuation attenuates with a very small decrement, and this should be a precursor of the presence of pulsating propagation of the phase-transition front. Similar regimes are well known in combustion theory.[4]

A more detailed analysis of these questions is beyond the scope of the considered instability of stationary propagation of a PT front.

b) We finally consider briefly the question of morphological instability in the quasistationary approximation, i.e., neglecting the inertia of the heat dissipation. In this approximation we must put $\varepsilon=\varepsilon_q$ in the general expression (16). It follows then from (26) that in the FMS the numerator is always positive, so that the stability condition reduces to the requirement that the denominator be positive

$$\mu<(A+\varepsilon)^{1/2}. \tag{38}$$

The least stable are long-wave propagations of the front ($q\to 0$) for which the condition (38) takes the form $\mu<\tilde{\mu}\equiv\sqrt{A}$ (see Fig. 7). It is interesting to note that in the quasistationary approximation the surface tension does not enter in the criterion of the morphological stability (this correlates with the conclusion that the least stable are perturbations with $q=0$), as well as that the instability threshold at large A ($\nu^2 \gg 1$) (the only case when the quasistationary treatment is valid) agrees, accurate to $1/A$, with the threshold of the thermal instability considered in item *a*) ($\mu_0 = (1+\nu^{-2})\tilde{\mu}$). All this can be apparently interpreted to mean that the morphological instability in the quasistatic limit ($\nu\to\infty$) is indeed a manifestation of the thermal instability of the one-dimensional problem.

To conclude this section we note that a complete analysis of the morphological instability of fast regimes ($\nu\sim 1$; $\varepsilon_q\sim\varepsilon_\Omega\sim 1$) calls for a separate treatment, in view of the substantial role of the nonstationary effects.

§4. CONCLUSION

We have presented a consistent theoretical analysis of the feasibility of stationary motion regimes of a plane phase-transition front in the FMS and investigated their stability.

Simultaneous account of the exothermy of the FMS phase transition into a stable phase and of the finite rate of heat dissipation reveals the possibility of thermal instability of the "explosive" type for the velocity of the PT front. We calculated the critical parameters of this instability as functions of the intensity of the heat dissipation and of the parameters that determine the thermal stability of the FMS. The onset of such an instability can be qualitatively understood if it is recognized that, generally speaking, a finite heat-dissipation rate still does not lead by itself to instability of the PT front (even without allowance for the stabilizing influence of the surface tension on the phase separation boundary). Only sufficiently poor heat dissipation in conjunction with positive feedback that is peculiar just to FMS can lead to loss of stability. The physical meaning of the stability criteria obtained by us (which is particularly lucid in the quasistationary approach) reduces therefore to the fact that if the change of the heat release on the PT front following a small change of the front temperature exceeds the corresponding change of the heat-dissipation rate, the stationary state in question (corresponding to equality of the heat release and heat dissipation) is unstable, and vice versa.

We now dwell briefly on the possibility of using the results of our study to interpret the experimental data on the thermal stability of FMS in the solid state. It must be borne in mind here that this use is justified if the main contribution to the investigated effects is made by the appreciable exothermy of the transition of the FMS into a stable phase, and the influence exerted on the PT velocity by stresses that occur in the course of the transitions and not accounted for in this paper can be neglected for some reason or another. This are primarily cases when the density of the medium changes little in the PT, as well as when the stresses arising in the course of motion of the PT front have time to relax on account of plastic deformation. One might think this relaxation to be effective both in the case of low velocities of the PT front, which is natural, and in the case when fast regimes are realized and the appreciable temperature rise on the PT front, considered in this paper, increases substantially the rate of this relaxation.

The most direct use of the equations derived in this paper is for the interpretation of experiment on the propagation of the crystallization front in sufficiently long and narrow films of amorphous substances, when a fast crystallization regime is excited via local heating of the film in one way or another. This includes also the known experiments on "explosive" crystallization of amorphous films.[5,6]

We list now, finally those of our results which are of greatest importance for experiments.

1. The feasibility of fast motions of the PT front as a result of considerable self-heating of the front, a feature peculiar to FMS.

2. The hysteresis in the dependence of the observed PT front velocity u as a function of the substrate temperature. Under certain conditions breaks can appear on the $u(T_0)$ plot when the motion along the upper branch is stable even at $T_0=0$.

3. The existence of "critical" parameters (substrate temperature, film thickness, and others) that determine the limits of thermal stability.

4. In some cases in the fast regime, the loss of

thermal stability can be oscillatory.

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[1)]Therefore, in particular, the entropy of such states does not satisfy the Nernst theorem at $T=0$ and remains finite.

[2)]We note, however, that some of the results that follow (particularly in § 3) are valid also for a function $u(T)$ of more general form than (1).

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