# Instability of a plane crystallization front in a dilute solution

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(Submitted 20 April 1983; resubmitted 3 June 1983)
Zh. Eksp. Teor. Fiz. **85**, 1743–1747 (November 1983)

The problem of the stability of a steadily moving plane isothermal crystallization front in a dilute solution is considered with allowance for inclusion of solute molecules in the solid phase. The local rate of motion of the phase boundary is determined by a kinetic equation of the Onsager type with allowance for surface tension. It is shown that if the coefficient for inclusion of the solute in the solid phase is smaller than a certain critical value that decreases with increasing value of the surface tension coefficient, the plane front will be aperiodically unstable against two-dimensional long-wavelength perturbations.

PACS numbers: 82.60.Nh, 82.60.Lf

The instabilities of nonequilibrium phase-transition fronts are now being extensively studied, both experimentally and theoretically.[1] One of the most important examples is the crystallization of a supercooled melt.[2,3] A widely used approach to the theoretical description of this process is based on a treatment of the Stefanov problem,[4] in which it is assumed that the temperature $T_0$ at the crystallization front remains constant during the crystallization of a one-component melt, and that the concentration $c_0$ at the front remains constant in the isothermal crystallization of a binary melt. A more realistic assumption concerning the kinetics of the phase transition was used in Ref. 5 (also see Ref. 6), where it was assumed that the crystallization rate is proportional to the difference between the chemical potentials of the substance in the liquid and solid phases in the case of the crystallization of a slightly supercooled melt. Our approach, however, differs from that of Ref. 5 in that we assume the solution to be dilute (and not close to the eutectic point) and consider not only one-dimensional perturbations, but also multidimensional perturbations (which lead to a curved front).

Let us write the diffusion equation for the solute in the comoving coordinate system in which the crystallization front, which moves in the laboratory system with velocity $V$, is at rest:

$$\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial z^2}+D\frac{\partial^2 c}{\partial y^2}+V\frac{\partial c}{\partial z}, \tag{1}$$

where $D$ is the diffusion constant, $c$ is the solute concentration ($c \ll 1$), the coordinate $z$ is directed into the melt (the plane front lies at the point $z = 0$), and the coordinate $y$ lies in the front. We neglect the diffusion of the solute in the solid phase. We shall assume that at the phase boundary the concentration $c_s$ in the solid phase is proportional to the concentration $c_1$ in the liquid phase:

$$c_s=\alpha c_l, \tag{2}$$

where $\alpha$ is the distribution coefficient[2] ($\alpha \leqslant 1$).

To obtain an equation for the crystallization rate we write down the values of the chemical potentials $\mu_l$ and $\mu_s$ of the solvent and $\mu_l'$ and $\mu_s'$ of the solute, where the indices $l$ and $s$ refer to the liquid and solid phases, respectively[7]:

$$\mu_l=\mu_l^{(0)}-Tc_l,\quad \mu_s=\mu_s^{(0)}-Tc_s, \tag{3}$$

$$\mu_l'=T\ln\frac{c_l}{e}+\psi_l,\quad \mu_s'=T\ln\frac{c_s}{e}+\psi_s. \tag{4}$$

Here $\mu_l^{(0)}$ and $\mu_s^{(0)}$ are the chemical potentials of the pure solvent in the liquid and solid phases, $\psi_l$ and $\psi_s$ are the concentration-independent terms in the chemical potentials of the solute, $T$ is the temperature (Boltzmann's constant is taken equal to unity), and $e$ is the base of the natural logarithms. We shall take account of the fact that, in accordance with Eq. (2), each solvent molecule passing from the liquid to the solid phase brings with it $\alpha c_l$ solute molecules. Then from Eqs. (3) and (4) we obtain the effective energy $E$ released when a single solvent molecule passes from the liquid to the solid phase:

$$E=\Delta\mu^{(0)}-Tc_l(1-\alpha-\alpha\ln\alpha^{-1}), \tag{5}$$

where $\Delta\mu^{(0)}=\mu_l^{(0)}-\mu_s^{(0)}$. In what follows we shall write $\beta\equiv 1-\alpha-\alpha\ln\alpha^{-1}$ (it is easy to see that $\beta\geqslant 0$ when $\alpha\leqslant 1$). In the weakly nonequilibrium situation we are considering $E$ plays the part of a thermodynamic force, while the flux associated with it is the flux of solvent passing from the liquid to the solid phase. If the density of the solvent is taken as unity and the difference between the densities of the two phases is neglected, this flux will be equal to $V$. In the linear approximation, the flux and force are connected by the Onsager relation[7]

$$V=\gamma E=\gamma(\Delta\mu^{(0)}-T\beta c_l), \tag{6}$$

where $\gamma$ is the phenomenological kinetic coefficient. Equations (5) and (6) hold for the case of a plane phase boundary. In considering the evolution of a multidimensional perturbation we shall have to deal with a curved phase boundary whose position $\zeta(t, y)$ is given by the equation

$$\zeta(t,y)=z_1e^{\Gamma t}\sin ky, \tag{7}$$

in which $\Gamma$ is the logarithmic growth rate of the instability, while $k$ and $z_1$ are the wave number and amplitude of the perturbation. In this case the contribution of the surface tension to the chemical potential must be taken into account in Eq. (5), while the flux in Eq. (6) must be taken as the component $V_n$ normal to the boundary. The surface-energy density is proportional to the curvature of the surface, which, in the approximation linear in the perturbation (7), is given approximately by

$$\frac{\partial^2\zeta}{\partial y^2}=-z_1k^2e^{\Gamma t}\sin ky.$$

When this is taken into account, Eq. (6) assumes the form

$$V_n=\gamma\Delta\mu^{(0)}-\gamma\beta Tc_l-\sigma k^2z_1e^{\Gamma t}\sin ky, \tag{8}$$

in which $\sigma$ is proportional to the product of $\gamma$ by the surface tension coefficient.

Equations (1) and (6) must be supplemented by the condition

$$-D\frac{\partial c}{\partial n}=V_nc_l(1-\alpha), \tag{9}$$

which results from the conservation of matter; here $\partial c/\partial n$ is the normal component of the concentration gradient at points of the phase boundary [Eq. (9) means that at the boundary the solute diffusion flux is equal to the drift flux].

Equation (1) with the boundary conditions (6) and (9) has an obvious stationary solution that describes the motion of the plane front with the constant velocity $V_0$:

$$c^{(0)}(z)=c_0+c_{01}\exp\left[-\frac{V_0}{D}z\right], \tag{10}$$

where $c_0$ is the concentration at infinity,

$$c_{01}=\frac{1-\alpha}{\alpha}c_0; \tag{11}$$

$$V_0=\gamma(\Delta\mu^{(0)}-\beta T\alpha^{-1}c_0). \tag{12}$$

We note that this solution is meaningful only when $V_0>0$ [otherwise the concentration, according to (10), would increase exponentially with increasing distance from the front in the liquid phase]; that is, as is evident from (12), the solution is meaningful only when $\alpha>\alpha_0$, where $\alpha_0$ is defined by the transcendental equation

$$\frac{\Delta\mu^{(0)}}{Tc_0}\alpha_0=1-\alpha_0\ln\alpha_0^{-1}-\alpha_0. \tag{13}$$

On considering the stability of the solution (10)–(12), we must note at once that multidimensional perturbations, which are associated with curvature of the front, must lead to aperiodic instability. Indeed, as is evident from (10)–(12), a stationary solution is characterized by a concentration that decreases monotonically with increasing distance from the front in the liquid phase. Hence, if a convex region arises on the front as a result of the perturbation it will penetrate into a region of lower concentration where, according to (6), its velocity will increase and it will become even more convex. Similarly, a concave region that lags behind the front will lag even further. We note that a similar mechanism for the aperiodic instability of a plane front is well known in the theory of gas flames,[8] in the theory of laser vaporization,[9] and in other problems. Such instability may be called kinetic instability. In the Stefanov problem as treated with allowance for surface tension,[3,4] another instability, which may be called diffusion instability, was discovered. This instability is related to the fact that in the Stefanov formulation the propagation velocity of the transformation front is determined solely by the solute outward diffusion rate; then the concentration gradient ahead of a convex region of the front increases, so that the solute leakage rate increases and the convex region moves faster and becomes more convex. In our case both the kinetic and diffusion mechanisms contribute to the instability. To obtain a quantitative description of these mechanisms we introduce a perturbed boundary of the form (7), and to determine the perturbation of the concentration field we substitute the perturbed concentration of the form

$$c(t,y,z)=c^{(0)}(z)+e^{\Gamma t}\tilde{c}(z)\sin ky, \tag{14}$$

[here $\tilde{c}(z)\sin ky$ is the eigenmode of the perturbation corresponding to the wave number $k$] into Eq. (1) with $V=V_0$. A simple calculation yields

$$\tilde{c}(z)=c_1\exp[-\varkappa(k)z], \tag{15}$$

where $\tilde{c}_1$ is the amplitude of the perturbation and

$$\varkappa(k)=\frac{1}{2D}\{V_0+[V_0^2+4D(Dk^2+\Gamma)]^{1/2}\}. \tag{16}$$

After linearizing the boundary conditions (8) and (9) with respect to the boundary perturbation (7) and the concentration perturbation (14)–(16), we obtain from the condition that the two homogeneous linear equations for the amplitudes $z_1$ and $c_1$ be compatible the following dispersion equation that determines the logarithmic increment $\Gamma(k)$ of the instability:

$$(\varepsilon-\xi+\tau k^2)[1+\theta k^2+4\varepsilon]^{1/2}=(1-2\xi-2\alpha)\varepsilon+(1-2\alpha)\tau k^2-\xi, \tag{17}$$

where

$$\theta=4D/V_0^2,\quad \tau=\sigma D/V_0^2,\quad \xi=\gamma\beta Tc_{01}/V_0,\quad \varepsilon=D\Gamma/V_0^2. \tag{18}$$

To determine whether Eq. (17) has roots that satisfy the instability condition $\varepsilon>0$, we note, first, that all the roots of this equation are negative in the limit $k^2\to\infty$:

$$\varepsilon_1\approx-\tau k^2,\quad \varepsilon_2\approx-\frac{1}{4}\theta k^2. \tag{19}$$

As is evident from the definitions (18) of $\tau$ and $\theta$, this is associated with the obvious fact that the surface tension and diffusion must necessarily suppress the high-frequency perturbations in the limit as $k^2\to\infty$. As is easily seen, the branch $\varepsilon_1$ corresponds to the natural perturbation which, in the limit as $k^2\to\infty$, is expressed through curvature of the boundary against the background of the unperturbed concentration field, while the branch $\varepsilon_2$ corresponds to perturbation of the concentration at a plane boundary.

Equation (17) simplifies when $k^2=0$, becoming1)

$$(1+4\varepsilon)^{1/2}-1=\left(2+\frac{(1+4\varepsilon)^{1/2}-1+2\alpha}{\xi}\right)\varepsilon. \tag{20}$$

This equation has the obvious root $\varepsilon=0$. When $\varepsilon>0$, however, $(1+4\varepsilon)^{1/2}-1<2\varepsilon$, while $(1+4\varepsilon)^{1/2}-1+2\alpha>0$; hence Eq. (20) has no positive roots. It is also easy to see that Eq. (20) has no complex roots with positive real parts, which means that the stationary solution is stable against one-dimensional perturbations.

Thus, if the logarithmic increment is positive in some wave-number region there should be a value $k_0^2$ of $k^2$ at which the logarithmic increment changes sign, i.e., for which $\varepsilon(k_0^2)=0$. On substituting $k^2=k_0^2$ and $\varepsilon=0$ in (17) we find, after simple calculations, that when

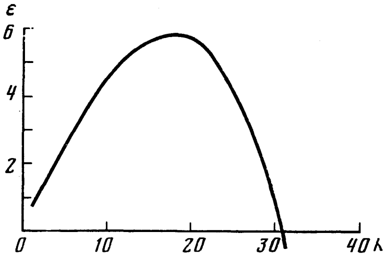

FIG. 1. The logarithmic increment $\varepsilon$ of the instability vs the wave number $k$ of the perturbation as calculated with Eq. (17) using typical values of the parameters.

$$\xi\theta<4\alpha\tau \tag{21}$$

the equation obtained for $k_0^2$ has no positive real roots, and when

$$\xi\theta>4\alpha\tau \tag{22}$$

it has one positive root:

$$k_0^2=\{\xi\theta+2\alpha\tau-2[\alpha\tau(\alpha\tau+2\xi\theta)]^{1/2}\}/\tau\theta. \tag{23}$$

In particular, it is easy to write down an approximate expression for the root of Eq. (17) that is valid in the region of small $k^2$ values:

$$\varepsilon(k^2)\approx\frac{\xi\theta-4\alpha\tau}{4\alpha}k^2. \tag{24}$$

If Eq. (22) is satisfied, a typical dependence of $\varepsilon$ on $k^2$ has the form shown in Fig. 1 [the figure is based on the results of a numerical solution of Eq. (17) for the parameter values $\alpha=0.5$, $\xi=10^3$, $\theta=1$, and $\tau=1$; the parabolic dependence (24) holds only for small $k^2$ values and is not shown on the figure since it is valid only in the region $k\lesssim10^{-3}$ for the parameter values chosen for the calculations].

If we use Eqs. (18) to rewrite the instability condition (22) in terms of the initial parameters, it takes the form

$$\gamma\beta Tc_{01}>\alpha V_0\sigma. \tag{25}$$

Since $\sigma$ occurs in (25) and $D$ does not, it is clear that the branch of the $\varepsilon(k)$ function depicted in Fig. 1 [which exists when condition (25) holds] passes over into the branch $\varepsilon_1(k)$ defined in (19) in the limit as $k^2\to\infty$.

If Eq. (17) had complex roots with positive real parts the plane front would become unstable. Numerical calculations show, however, that there are no such roots.[2] Thus, a steadily moving plane crystallization front in a dilute supercooled solution is stable, according to Eq. (21), provided the distribution coefficient is not too small, i.e., provided the solid and liquid phases do not differ too much in composition. The critical value $\alpha_*$ of the distribution coefficient is determined by the transcendental equation obtained by substituting expressions (11) and (12) for $c_{01}$ and $V$ into (25) and changing the inequality sign to an equal sign; it has the form

$$c_0T\beta_*(1-\alpha_*)=\alpha_*(\Delta\mu^{(0)}-\beta_*Tc_0)\sigma, \tag{26}$$

where $\beta_*=1-\alpha_*-\alpha_*\ln\alpha_*^{-1}$. It is easy to see that Eq. (26) has precisely one positive root and that that root lies in the interval $\alpha_0<\alpha_*<1$ [$\alpha_0$ is defined by Eq. (13)]. Thus, if $\alpha$ lie in the range

$$\alpha_0<\alpha<\alpha_*,$$

the plane front will be aperiodically unstable against perturbations with wave numbers $k^2<k_0^2$.

The authors thank M. B. Geĭlikman, É. N. Rumanov, M. I. Tribel'skiĭ, and A. A. Chernov for valuable discussions, and Ya. B. Azarov for assistance with the numerical calculations.

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[1] In treating one-dimensional perturbations (i.e., perturbations with $k^2=0$) one may introduce the perturbation of the position of the phase boundary, as was done above, or one may regard the boundary as lying in the plane $z=0$, as before, and introduce the perturbation of the velocity: $V(t)=V_0+V_1e^{\Gamma t}$. The second approach also leads to Eq. (20).

[2] As was noted above, this assertion can be rigorously proved for the case $k=0$, when Eq. (17) reduces to Eq. (20).

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Translated by E. Brunner