Explosive nonisothermal growth of a spherical phase-transition center during the decay of frozen metastable states

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The quasisteady growth of a spherical center of a stable phase in a massive sample, with heat evolution at the phase-transition front, is shown to exhibit self-accelerated growth and can occur explosively. The minimum heat evolution at the phase-transition front required for a thermal explosion of the center is calculated as a function of the initial temperature of the sample. Expressions for the lower and upper critical radii and for the duration of the heating before the explosion are derived and discussed.

INTRODUCTION

A problem of particular interest for configurationally frozen metastable states, the most characteristic examples of which are amorphous substances (glasses), is that of determining the conditions under which these states are thermally stable with respect to a transition to a stable macroscopic phase during uniform or local heating. The interest stems primarily from the thermal instability of a phase-transition front, which can occur in a configurationally frozen metastable state.[1] This instability gives rise to an explosive propagation of the front, in the course of which the rate of the transition of the sample to the stable phase can increase sharply due to even a relatively small change in the parameters of the problem.

With respect to the thermal instability of a spherical phase-transition center in a massive sample of a configurationally frozen metastable state — the problem with which we are concerned in the present paper — the later observation means that for certain values of the temperature of the sample and of the heat evolution at the front there exists an interval of radii of the growing center in which the center is a bistable system. In other words, two different stable values of the velocity (and, correspondingly, the temperature) of the front are possible. The results of numerical calculations on this instability of a spherical center were reported in Ref. 3 in connection with an explanation of experiments on the explosive crystallization of amorphous H_2O (Ref. 2; the heat evolution at the front was not taken into account in a completely systematic way).

Our purpose in the present paper is to analyze the possibility of an explosive growth of a spherical front for arbitrary values of the heat evolution at the front and of the temperature of the medium. We will also derive the corresponding values of the critical radius and the duration of the heating before the explosion. Qualitatively similar problems are quite well known in the theory of combustion and thermal explosions (Ref. 4, for example), but in the formulation of the problem used in that field (in most cases, it is assumed that there is no sharp "reaction front") an analytic study requires many approximations.

In Section I we discuss the formulation of the problem of the nonisothermal growth of a spherical phase-transition center in the quasistatic approximation. In Section 2 we determine the region in which explosive growth occurs. In Section we calculate the critical radii and the duration of the heating before the explosion in the direct heat removal approximation. In Section 4 we discuss possibilities for experimental observation, and we state our conclusions.

§1. STATEMENT OF THE PROBLEM

A spherical center of a stable phase of radius $R(t)$ is growing in a metastable phase with an initial temperature $T_0 > T_t$, where T_t is the temperature of the equilibrium phase transition. The temperature field $\theta(r, t)$, measured from T_0, around a center of this type is described by the heat-conduction equation

$$\frac{1}{\varkappa}\frac{\partial\theta}{\partial t}=\frac{\partial^2\theta}{\partial r^2}+\frac{2}{r}\frac{\partial\theta}{\partial r}, \tag{1}$$

whose solution must be finite at $r = 0$, must be continuous at $r = R(t)$, must vanish in the limit $r\to\infty$, and must satisfy the heat-balance condition at the front:

$$T_Q\dot{R}=\varkappa(\nabla\theta'-\nabla\theta)|_{r=R(t)}. \tag{2}$$

Here $\varkappa$ is the thermal diffusivity, $T_Q \equiv Q/c$, where Q is the latent heat of the phase transition, c is the specific heat, a primed quantity refers to the stable phase, and for simplicity we are assuming $\varkappa = \varkappa'$, $c = c'$.

As in our previous papers, we describe the kinetics of the phase transition at the interface by the following dependence of $u\equiv\dot{R}$ on the front temperature T_f, which is well known in the theory of crystallization[5]:

$$u(T_f)=u_0\exp\left(-\frac{E}{T_f}\right)\left\{1-\exp\left[-\Delta H\left(\frac{1}{T_f}-\frac{1}{T_t}\right)\right]\right\}, \tag{3}$$

where ΔH is the heat of the phase transition per atom at $T_f = T_t$, and the kinetic parameters u_0 and E, which determine the viscosity of the frozen phase, can be extracted from experiments on low-temperature ($T \ll T_t$), isothermal annealing of a sample in a configurationally frozen metastable state.[6]

The problem of self-consistently determining the evolution of the thermal field $\theta(r, t)$ and the coordinate $R(t)$ on the basis of Eqs. (1)–(3) is known to be very nonlinear and

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is complicated further by the time variation in Eq. (1). If, however, we ignore the inertia of the heat removal from the front [i.e., if we ignore the time derivative in Eq. (1), written in the rest frame of the front — see Ref. 7], we can easily derive a quasisteady solution of Eq. (1) for $\theta(r)$ which satisfies condition (2) and which depends parametrically on the time through $R(t)$ and $u\equiv\dot{R}(t)$:

$$\theta(r)=\theta_f(z),\quad r<R(t),$$
$$\theta(r)=\theta_f(z),\quad r<R(t),$$

where $z\equiv R/l\equiv Ru/\varkappa$,

$$E_2(z)\equiv\int_1^\infty \frac{dt}{t^2}e^{-zt},\qquad \theta_f(z)=T_Q z e^z E_2(z). \tag{4}$$

Expression (4) is yet another relation [supplementing (3)] between u and θ_f. It is analogous to Eq. (7) of Ref. 1a if we introduce a local rate of heat removal from the spherical front [see also Eq. (34) in Ref. 7]. We then write $z=\nu^{-1}\equiv u/v$, and we can easily show[8] that the functions $u(T_f)$ which follow from (4) behave, upon a variation of v, in qualitatively the same way as the analogous "heat-removal curves" in Fig. 2 in Ref. 1a. Specifically, as the sphere radius R is increased, the removal of heat from the sphere slows monotonically, and the heat-removal curve sags downward and to the right, remaining at all times in the band $T_0<T_f<T_0+T_Q$.

The problem of self-consistently calculating the rate of increase $\tilde{u}(R)$ of a spherical center with heat evolution at the front in the quasisteady approximation thus reduces, as in Ref. 1 and 7, to a joint algebraic analysis of two nonlinear equations, (3) and (4). Using the graphical method of Ref. 1, we can show that the qualitative behavior $\tilde{u}(R)$ for various relations among the parameters of the problem is analogous to the two-dimensional adiabatic case (see Figs. 8 and 9 in Ref. 7).

§2. DETERMINATION OF THE REGION IN THE (τ_0, τ_Q) PLANE IN WHICH EXPLOSIVE GROWTH OCCURS

We turn now to a quantitative analysis of explosive growth, i.e., of those cases in which the dependence $\tilde{u}(R)$ becomes multivalued in a certain interval of the parameters of the problem (see also Fig. 9, b and c, in Ref. 7). We will restrict the discussion to cases in which the "nucleating" kinetic curve (3) can be represented accurately by $u(T_f)=u_0\exp(-E/T_f)$ (Refs. 1 and 7).

Transforming to the dimensionless variables $w\equiv u/u_0$ and $\tau\equiv T/E$, we can write Eqs. (3) and (4) as

$$w=\exp(-1/\tau), \tag{5}$$

$$\tau-\tau_0=\tau_Q\Psi(z), \tag{6}$$

where

$$z\equiv w/V,\quad V\equiv v/u_0,\quad \tau_0\equiv T_0/E,\quad \tau_Q\equiv T_Q/E,\quad \Psi(z)=ze^zE_2(z).$$

To determine the critical radii of the growing center [i.e., those values of $R_c(\tau_0,\tau_Q)$ at which new branches of the function $\tilde{u}(R)$ appear, or old ones disappear] we make use of the circumstance that at $R=R_c$ not only the values of $w(\tau_c)$ given by (5) and (6) but also the values of the corresponding derivatives w'_τ must be equal. Using the identity $\Psi'_z=\Psi(1+2/z)-1$, which is easily verified, we can then show that we have

$$V_c=\exp(-1/\tau_c)/z_c, \tag{7}$$

where $V_c=\varkappa/u_0R_c$, and z_c and τ_c, which are functions of the parameters τ_Q and τ_0, are found from a system of two nonlinear equations, one being (6) and the other

$$z=(\tau-\tau_1)(\tau-\tau_2)/(\tau-\tau_3), \tag{8}$$

where

$$\tau_{1,2}\equiv1\mp(1-2\tau_0)^{1/2},\quad \tau_3\equiv\tau_0+\tau_Q.$$

Here and below, for simplicity, we omit the index c [which corresponds to the points of tangency of curves (5) and (6)] from τ and z. The determination of the points of tangency of curves (5) and (6) thus reduces to finding the points at which (6) and (8) intersects.

We will therefore analyze system (6), (8) in more detail, in order to identify those regions in the (τ_0, τ_Q) plane in which explosive growth can occur.

Since the only solutions of Eqs. (6) and (8) which are physically meaningful are those for which the conditions $z>0$ and $\tau>0$ hold, we easily see that the latter is possible if one of two inequalities of the form

$$\theta_1<\tau_Q<\tau_2, \tag{9}$$

$$\tau_Q>\theta_2 \tag{10}$$

holds. Here $\theta_{1,2}\equiv\tau_{1,2}-\tau_0$ [see also Fig. 1, where the function $\theta_1(\tau_0)$ is shown by the solid line and $\theta_2(\tau_0)$ by the dashed line]. If $\tau_Q=\theta_2$, expression (8) simplifies substantially:

$$z=\tau-\tau_1. \tag{11}$$

We will make use of this result below. The inequality $\tau_Q>\theta_1(\tau_0)$ along with the condition $\tau_0<1/2$ (see the expression for $\tau_{1,2}$) defines a region in the (τ_0, τ_Q) plane in which the function $\tilde{u}(R)$ is clearly single-valued (the oblique hatching in Fig. 1). In order to reduce still further the intervals of τ_0 and τ_Q in which the functions $\tilde{u}(R)$ may be multivalued, we need to pursue the graphical analysis of Eqs. (6) and (8) in the (z, τ) plane.

We find as a result that as the parameters τ_0 and τ_Q are

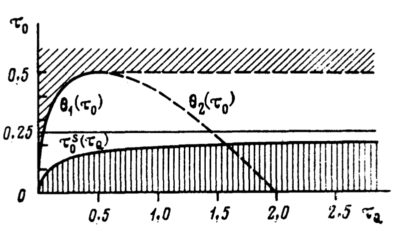

FIG. 1. The region of explosive growth in the (τ_0, τ_Q) plane lies between the line $\tau_0^s(\tau_Q)$ and the abscissa axis (the region with the vertical hatching).

varied independently the points at which the lines in (6) and (8) intersect generally — except in special cases in which these points coalesce — appear or disappear exclusively in pairs. These special (singular) cases of a coalescence of the intersections of curves (6) and (8), on the other hand, on the (τ_0, τ_Q) plane correspond to the line $\tau_0^s(\tau_Q)$, which separates single-valued growth from multivalued growth. Since the singular points in the (z, τ) plane are by definition the points of tangency of lines (6) and (8), we find from the equality of the derivatives $dz/d\tau$ at those points that we have

$$\tau^2(\tau^2-2\tau\tau_3+2\tau_Q)=(\tau-\tau_3)(\tau-\tau_2)(\tau-\tau_1). \qquad (12)$$

For simplicity here we have omitted the index s from τ and τ_0. The three equations (6), (8), and (12) determine singular values of three critical parameters (z^s, τ^s, and τ_0^s) as functions of the adjustable parameter τ_Q. However, since these equations are nonlinear, analytic results for $\tau_0^s(\tau_Q)$ can be found only at small values, intermediate values ($\tau_3=\tau_2$), and large values of the parameter τ_Q. We will briefly review the basic points and results of this analysis

a) $\tau_Q\to 0$ ($\tau_3<\tau_2$). We seek the equation of the line $\tau_0^s(\tau_Q)$ in the limit $\tau_0\to 0$. Assuming $\tau_Q\sim\tau_0^2$ and $\theta\equiv\tau-\tau_0\sim\tau_0^2$ by analogy with the one-dimensional problem (where a similar result can be derived explicitly), we can write Eq. (12) as follows, with an accuracy to terms of order τ_0^4:

$$2\theta^2-\theta(\tau_0^2+2\tau_Q)+3\tau_Q\tau_0^2-\tau_0^4=0. \qquad (13)$$

Introducing x by means of the relation $\tau_Q\equiv x\tau_0^2$, we find from (13)

$$\theta_\pm\equiv\lambda_\pm(x)\tau_0^2, \quad \lambda_\pm(x)=[1+2x\pm(4x^2-20x+9)^{1/2}]/4, \qquad (14)$$

with $x>9/2$. With the same accuracy, we find from (8)

$$z_\pm\approx(2\lambda_\pm-1)/(x-\lambda_\pm), \qquad (15)$$

and Eq. (6) becomes

$$\Psi(z_\pm)=\lambda_\pm/x. \qquad (16)$$

The problem of determining x has thus been reduced to one of solving Eqs. (15) and (16) jointly. After plotting the function $z_\pm(x)$ and $\lambda_\pm(x)$, we can prove that solutions exist at $x>9/2$ [corresponding to only the plus sign in (14)–(16)]. We thus verify our original assumption regarding the relationship between τ_0 and τ_Q at $\tau_0\ll 1$. We skip over the corresponding lengthy analysis (which must be carried out, however, for a numerical determination of x) to the final result: $x\approx 5.44$.

b) $\tau_3=\tau_2$, i.e., $\tau_Q=\tau_2-\tau_0$. In this case we are on the line $\theta_2(\tau_0)=\tau_Q$. Expression (8) reduces to (11), while (12) simplifies considerably

$$\tau^2-\tau+\tau_1=0. \qquad (17)$$

It can be shown that the problem of solving the system of equations (6), (11), (17) reduces to the problem of solving the single transcendental equation

$$\Psi(z)=z[2+(1-z^{1/2})^2][7/4+(z^{1/2}-1/2)^2]^{-2}, \qquad (18)$$

$$z=z(\tau_0)\equiv\tau^2=[1-(1-4\tau_1)^{1/2}]^2/4. \qquad (19)$$

A numerical solution of (18) yields $z\approx 0.12$, also using (19), we find $\tau=0.35$ and $\tau_0=0.20$.

c) $\tau_3>\tau_2$ ($\tau_Q\to\infty$). In this case it is convenient to replace Eq. (12) by an equation which relates τ and z at the singular points. Since (8) and (6) give us

$$dz/d\tau=[2(\tau-1)-z]/(\tau-\tau_3), \quad dz/d\tau=z/\tau^2,$$

by eliminating $dz/d\tau$ we find

$$2\tau=2+z+[1+2\Psi/z(\Psi-1)]^{-1}. \qquad (20)$$

In the limit $\tau_Q\to\infty$, which corresponds to $z\to 0$, we then have

$$\Psi(z)\approx z(1+z\ln z), \qquad (21)$$

and from (20) we easily find

$$\tau=1/2+z\ln z. \qquad (22)$$

Substituting (21) into (6), and substituting (22) into (8), we find

$$z\approx\varepsilon(1+\varepsilon\ln\varepsilon), \qquad (23)$$

where $\varepsilon\equiv 1/4\tau_Q\ll 1$. From (22) and (23) we find

$$\tau_0\approx 1/4(1+3\varepsilon\ln\varepsilon). \qquad (24)$$

Expressions (22)–(24) give us the asymptotic ($\varepsilon\to 0$) solution of system (6), (8), (20) which we have been seeking.

We thus find the following asymptotic results for the line $\tau_0^s(\tau^Q)$ which bounds the region of explosive growth in the (τ_0, τ_Q) plane:

$$\tau_0^s\approx(\tau_Q/x)^{1/2}, \quad \tau_Q\to 0,$$

$$\tau_0^s\approx 1/4(1+3\varepsilon\ln\varepsilon), \quad \tau_Q\to\infty.$$

Also shown in Fig. 1 is a curve of $\tau_0^s(\tau_Q)$ found through numerical analysis of the system (6), (8), (12). We see that the asymptotic behavior in (24) gives a very accurate description of the function $\tau_0^s(\tau_Q)$ at large values of τ_Q, up to the point of intersection with the line $\theta_2(\tau_0)$ (Fig. 1).

§3. DURATION OF THE PRE-EXPLOSION HEATING IN THE "DIRECT HEAT REMOVAL" APPROXIMATION

It would be impossible to analyze Eqs. (6) and (8), which give the coordinates of the points of tangency of the functions $w(\tau)$ and the heat-removal curve, in the general case because of the transcendental nature of $\Psi(z)$; numerical calculations would be necessary. There is, on the other hand, a simple and important case in which this analysis simplifies considerably. Specifically, if $z\ll 1$, we have $\Psi(z)\approx z$, and in this case the heat-removal curve (6) becomes the heat removal line

$$z=(\tau-\tau_0)/\tau_Q, \qquad (25)$$

and Eq. (8) gives us

$$\tau^2=\tau-\tau_0, \qquad (26)$$

from which we find

$$\tau_\pm=1/2[1\pm(1-4\tau_0)^{1/2}]. \qquad (27)$$

Using (7), we find

$$\rho_\pm=(\tau_\pm^2/\tau_Q)\exp\tau_\pm^{-1}, \tag{28}$$

where $\rho_\pm$ are the dimensionless (expressed in units of $l_0\equiv\varkappa/u$) upper and lower critical radii of a growing center from given values of τ_0 and τ_Q; the condition $\rho_+<\rho_-$ holds at all times.[7]

For the duration t_i of the heating before the explosion (this time interval is analogous to the "induction time" in the theory of the thermal explosion[4]), we easily find the following expression, using (25), (26), and $z\equiv\rho w$

$$t_i=\int_{\tau_0}^{\tau_-}\frac{d\tau}{w}\frac{d\rho}{d\tau}=\frac{1}{\tau_Q}\int_{\tau_0}^{\tau_-}d\tau\, e^{2/\tau}\left[1-\frac{\tau-\tau_0}{\tau^2}\right]. \tag{29}$$

This integral can be expressed in terms of special functions.[8] A physically interesting result, however, can be found more quickly from (29) in the case in which the heating before an explosion, $\delta\tau\equiv\tau_--\tau_0$, is small($\delta\tau\ll\tau_0$). Here it is sufficient that the inequality $\tau_0\ll1/4$ hold (for in this case we have $\delta\tau\approx\tau_0^2$), as follows from (27). Switching to the new variable $x\equiv(\tau-\tau_0)/\tau_0^2$ in the integral in (29), we finally find

$$t_i\approx(\tau_0^2/\tau_Q)Je^{2/\tau_0}, \tag{30}$$

$$J\equiv\int_0^1 dx(1-x)e^{-2x}={}^1/_4(1+e^{-2})\approx{}^1/_4.$$

It follows from (30) that at $\tau_0\ll1$ the time interval t_i is determined primarily by the exponential function, while the coefficient of the exponential function is proportional to $\delta\tau\ll1$.

It is also interesting to compare the expressions for the lower critical explosive radius ρ_- in (28) and t_i in (30). We find

$$\rho_-^2=Dt_i, \tag{31}$$

where $D\equiv4\tau_0^2/e^2\tau_Q$. Relation (31) clearly emphasizes the diffusive nature of the coupling of ρ_- with t_i, which follows from the diffusion mechanism for heat propagation from a growing center.

What is the range of applicability of the approximation of direct heat removal which we are using in this section?[1)] It turns out that the quantity $\rho_-(\tau_0)$ found from (28) in the limit $\tau_0\to0$ is a good approximation of the actual lower critical radius, calculated from (7), in the case $\tau_Q\gg\tau_Q(\tau_0^s)$. The condition for the applicability of the expression for $\rho_+(\tau_0)$ is more stringent: $\tau_Q\gg1$. We note, however, that in this approximation it is in principle impossible to find the minimum (for a given τ_0) heat evolution τ_Q which is required for the occurrence of explosive growth (§ 2), as can be seen formally just from the fact that the values of $\tau_\pm$ given by (27) are totally independent of τ_Q.

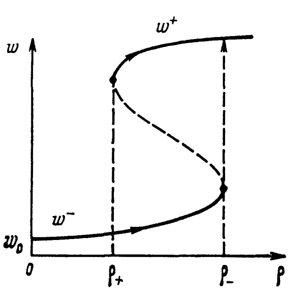

FIG. 2. Schematic plot of the front velocity w versus the radius ρ of the center for explosive growth (τ_0 and τ_Q are fixed). The dashed line shows the unstable branch of w; $\rho_\pm$ are the upper and lower critical radii; $w_0\equiv w(\tau_0)$.

CONCLUSION

Let us summarize this study. We have shown that at a constant temperature τ_0 of the medium a quasisteady growth of a spherical center of a stable phase in a configurationally frozen metastable state with heat evolution at the phase-transition front is always self-accelerated: The temperature at the front increases monotonically from τ_0 to $\tau_0+\tau_Q$, where τ_Q is the maximum heating. However, the growth of the center can occur in either of two ways, depending on the relation between τ_0 and τ_Q: a) If $\tau_0>\tau_0^s(\tau_Q)$ (Fig. 1), the function $w(\rho)$ is continuous and single-valued. b) If, on the other hand, $\tau_0<\tau_0^s(\rho)$, then for $\rho_+<\rho<\rho_-$, the front velocity $w(\rho)$ is a multivalued function (Fig. 2), so that as ρ increases the transition from the lower branch, $w^-(\rho)$, to the upper branch, $w^+(\rho)$, occurs in an explosive manner at $\rho=\rho_-$ (the region of explosive growth is shown by the vertical hatching in Fig. 1). The quantity ρ_+ in Fig. 2 is the smallest radius of a sphere which evolves in a quasisteady manner along the upper branch of the function $w(\rho)$ as a so-called hot center.[2,3] If the physical meaning of ρ_- can be seen even in the case of uniform heating, physical realization of ρ_+ is possible only in a time-varying experiment, with a spherical temperature T-burst of suitable intensity, duration, and initial dimension.[9]

Finally, we consider some possible ways for experimentally studying the explosive growth discussed above. In a transparent medium (a configurationally frozen metastable state in a dielectric, a liquid crystal, or a polymer), because of the difference between the optical properties of the stable and frozen phases, it would apparently be possible to directly observe the functions $w^\pm(\rho;\tau_0,\tau_Q)$ and $t_i(\tau_0;\tau_Q)$. In a metallic glass, where such an observation would not be possible, an effective and convenient method for controlling the growth of crystallization centers would be to use rapid heating of a bulk sample to a temperature τ_0 by passing a current pulse of the appropriate height and length through the sample. We might also mention some recent observations of hot crystallization centers in amorphous H_2O, which is a convenient model system for an experimental study of explosive growth, as Skripov and Koverda[3] have pointed out, because of the relatively low velocity of the hot crystallization front (low in comparison with that in metallic glasses).

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[1)]Similar arguments should hold for the one- and two-dimensional decay of a configurationally frozen metastable state, which has been studied previously[1,7] in the same approximation.

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