Eur. Phys. J. B **10**, 379–383 (1999)

THE EUROPEAN PHYSICAL JOURNAL B
EDP Sciences

Detonation type waves in phase (chemical) transformation processes in condensed matter

A. Pumir[1,a] and V.V. Barelko[2]

[1] Institut Nonlinéaire de Nice[b], 1361 route des Lucioles, 06560 Valbonne, France
[2] Institute of Chemical Physics, R.A.S., Chernogolovka, Moscow Region, Russia

Received 15 October 1998

Abstract. Fast self sustained waves (autowaves) associated with chemical or phase transformations are observed in many situations in condensed matter. They are governed neither by diffusion of matter or heat (as in combustion processes) nor by a travelling shock wave (as in gaseous detonation). Instead, they result from a coupling between phase transformation and the stress field, and may be classified as gasless detonation autowaves in solids. We propose a simple model to describe these regimes. The model rests on the classical equations of elastic deformations in a 1-dimensional solid bar, with the extra assumption that the phase (chemical) transformation induces a change of the sound velocity. The transformations are assumed to occur through a chain branched mechanism, which starts when the mechanical stress exceeds a given threshold. Our investigation shows that supersonic autowaves exist in this model. In the absence of diffusion (dissipation factor, losses), a continuum of travelling wave solutions is found. In the presence of diffusion, a steady state supersonic wave solution is found, along with a slower wave controlled by diffusion.

PACS. 82.20.Mj Nonequilibrium kinetics – 05.70.Ln Nonequilibrium and irreversible thermodynamics

Phase transformations or chemical reactions lead in extended systems to propagating travelling waves, whereby the stable phase invades the metastable phase [1,2]. The propagation regime may be controlled by a diffusive transfer of matter or heat. Such is the case in a number of problems originating from physics, chemistry (in particular, in combustion [3–5]), or even in biology [6]. The corresponding phenomena are governed by diffusion or heat conductivity equations which have been extensively investigated. Faster propagation regimes have also been recognized: in the context of gaseous detonation, the phenomena result from a coupling between combustion (chemistry) and gas compression (mechanics), leading to self-sustained supersonic waves [3,4].

Fast propagation of chemical and phase transformations also occur in a number of situations, involving condensed phases (contrary to detonation, which occurs in gaseous phases). Fast decomposition of a metastable phase has been observed in glassy semiconductors and metals, as well as in a geological context [7,8]. The "Prince Rupert drops", and more generally, tempered glasses, which explode as a result of a mechanical stimulation [9,10] is certainly a very spectacular example, which has remained a mystery for several centuries. Studies of detonation of classical solid explosives (such as heavy metal azides), also reveal the existence of a fast propagation regime in solid matrices, before the gas explosion stage [11].

In a different context, it has been shown that chemical waves propagate at very low temperature [12,13] and at usual temperatures [14] at rather high velocities, due to a coupling between chemistry and mechanical deformations. This phenomenon may be important to understand the abundance of certain molecules (ammonia or methane) in cold planets.

A related phenomenon occurs when an overheated liquid is vaporized: depending on the precise conditions, a slow wave, governed by diffusion, or a faster, more violent wave (hence the term "detonation boiling" [15]) may propagate.

In the phenomena listed above, the coupling between the stress field and the chemical reaction has been demonstrated to be of prime importance: propagation is *not* controlled by diffusion. The front velocity appears to be very high, of the order of the sound velocity in some cases. We note here that the strain field has been shown to be important in the (slow) kinetics of some morphological transitions in crystals and alloys [16,17].

The goal of the present letter is to introduce a simple model with an explicit coupling between phase (chemical) transformation in solids and the stress field. Our purpose at this stage is to propose a theoretical framework to describe the phenomena previously introduced. Qualitatively, the mechanism of propagation works in

---

[a] e-mail: `pumir@inln.cnrs.fr`

[b] CNRS

the following way. Once the reaction starts at one point, typically through a chain branched process, the main assumption is that the local stress is modified. This local modification of the stress propagates towards neighbouring regions, which results in a change of the local equilibrium of the reaction, and under proper conditions, in an initiation of the reaction. The phase transformation may therefore propagate from point to point, with a velocity of the order of the sound velocity. Note that similar ideas have been proposed in this context in [8]. Mathematically, this mechanism can be implemented by simply assuming a variation of the sound velocity in the medium, as a function of the order parameter of the reaction, as we now demonstrate.

In a solid, the evolution of the displacement field, $\mathbf{u}$, is given by Newton's law: $\rho \partial_t^2 u_i = -\partial_j \tau_{ij}$. In the context of linear elasticity theory the stress tensor, τ, is related to u by $\tau_{ij} \propto -E(\partial_i u_j + \partial_j u_i)$. Here, we consider a 1-dimensional simplified version of the problem, and neglecting some minor complications of elasticity theory, we write the evolution equation for u as:

$$\partial_t^2 u - \partial_x (V^2 \partial_x u) = 0 \qquad (1)$$

where the sound velocity, V, is such that $V^2 = E/\rho$, up to inessential constants.

In the problem considered here, the variable c describes the phase transformation (or the chemical reaction). We assume that c evolves according to a traditional chain branched process, described by the familiar kinetic function $f(c) = Ac^2(1-c) - kc$, $c = 0$ representing the metastable state. Equivalently, we use $f(c) = Ac(c_+ - c)(c - c_-)$ ($c_\pm = 1/2(1 \pm \sqrt{1 - 4k/A}$) [18]. Then,

$$\partial_t c = f(c) + D\partial_x^2 c + w(\partial_x u). \qquad (2)$$

A coupling term with the strain field, $w(\partial_x u)$, has been added to the usual diffusion equation for the concentration field, c. Physically, it is assumed that the system cannot stay in the metastable state when the strain field is too high (a possibility is that the phase transition starts when brittle destruction of the solid matrix occurs). Specifically, we assume that $w = 0$ when the strain $\partial_x u$ is lower than a threshold value, $(\partial_x u)_\mathrm{c}$. The term w is turned on when $\partial_x u$ exceeds $(\partial_x u)_\mathrm{c}$: $w(\partial_x u) = W_0$ for a time τ. If the constant W_0 is larger than the minimum of f, the metastable state in equation (2) becomes unstable, so the system moves towards its stable fixed point, see Figure 1. Another way of modelling this coupling consists in adding a fixed constant, $c_* > c_-$ to c when $(\partial_x u)$ becomes larger than $(\partial_x u)_\mathrm{c}$.

The diffusion term, D is assumed to be very small; we will be mostly concerned with the $D \to 0$ limit.

In addition, we assume that the sound velocity increases monotonically with c. On general grounds, it is reasonable to expect a dependence of $V^2 = E/\rho$ on c. The qualitative idea put forward earlier that the reaction modifies the stress suggests that E itself varies; we assume here that it increases with c. In addition, in the cases discussed in the introduction (with the notable exception of the "detonation boiling" problem) the phase transformation leads to a dilation of the medium ($\partial_x u$ increases, ρ decreases), making plausible the hypothesis that $V^2(c)$ increases monotonically with c. We simply use $V^2(c)$ in the model equation (1). The precise dependence of $V^2(c)$ is not crucial for the following discussion.

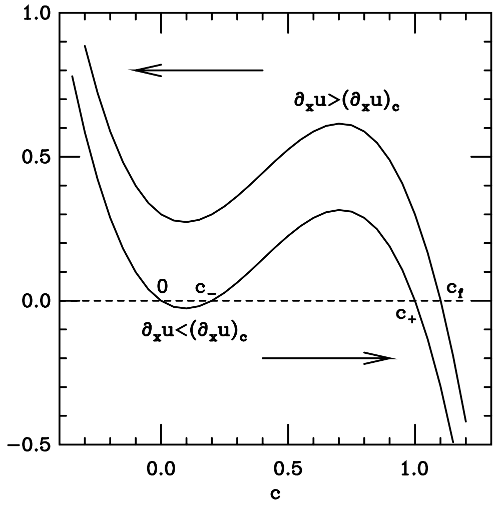


Fig. 1. Schematic representation of the function $f(c) + w(\partial_x u)$. The function $f + w(\partial_x u)$ is positive underneath the graphs. When the stress, $\partial_x u$, is lower than the critical value, $(\partial_x u)_\mathrm{c}$, the system can be either in the metastable state, $c = 0$, or in the stable state $c = c_+$. When the stress exceeds the critical value, the metastable state disappears, so the system moves towards the new stable state, $c = c_\mathrm{f}$.

Although equations (1, 2) are plausible, they clearly involve a number of simplifying assumptions. As we show in turn, the hypothesized coupling between c and the strain permits to reproduce a number of qualitative features of the fast phase transformations observed in nature.

We begin by observing that any state with a uniform value of $(\partial_x u) = (\partial_x u)_0$, and with $c = 0$ is a steady state. Because of the explicit coupling term $w(\partial_x u)$, a mechanical perturbation may induce a phase transformation. Similarly, a perturbation in c leads to a perturbation in the strain field. This can be seen by linearizing the equation of motion around the state $c = 0$ and $\partial_x u = (\partial_x u)_0$:

$$\partial_t^2 \delta u - V^2(0)\partial_x^2 \delta u = \frac{dV^2}{dc}(c = 0)\partial_x u_0 \partial_x \delta c. \qquad (3)$$

The right hand side of equation (3) is proportional to the perturbation in c, and acts as a source term for the elasticity equation.

We now investigate the existence of travelling wave solutions, corresponding to the stable state at $x \to -\infty$, invading the metastable state ($c = 0$ and $\partial_x u = (\partial_x u)_0$ when $x \to \infty$), so the front velocity is positive: $v_\mathrm{f} > 0$. It is convenient to introduce the comoving frame: $\xi = (x - v_{\mathrm{f}} t)$, leading to the equation of motion:

$$\partial_\xi \Big((V^2(c) - v_{\mathrm{f}}^2) \partial_\xi u \Big) = 0, \tag{4}$$

$$- v_{\mathrm{f}} \partial_\xi c = f(c) + D \partial_\xi^2 c + w(\partial_\xi u). \tag{5}$$

Equation (4) may be integrated once, leading to:

$$(V^2(c) - v_{\mathrm{f}}^2) \partial_\xi u = (V^2(0) - v_{\mathrm{f}}^2)(\partial_x u)_0. \tag{6}$$

Equation (6) shows that the stress may diverge, when at some point, $v_{\mathrm{f}}^2 = V(c_{\mathrm{e}})^2$. Our model certainly cannot be used to describe a situation where $\partial_\xi u \to \infty$. This feature suggests that the model should be modified, and that mechanical losses should be taken into account. In any event, the divergence does not occur when the front velocity is outside of the range of variation of the sound velocity in the material (*i.e.*, when either v_{f} is smaller than the sound velocity in the metastable phase, or v_{f} is larger than the sound velocity in the stable phase).

The limit $D \to 0$ is expected to be singular, since the diffusion term is the highest derivative term in equation (5). With this restriction in mind, we analyze first the $D = 0$ case.

The solution ahead of the front (for $\xi > 0$) is such that $c = 0$ and $\partial_\xi u = (\partial_x u)_0$. This can be seen by linearizing equation (5) in the metastable region ($\xi \to \infty$ and $c \approx 0$, $\partial_\xi u < (\partial_x u)_{\mathrm{c}}$), which leads to: $-v_{\mathrm{f}} \partial_\xi c = f'(0) \delta C$. The only non zero solution of this equation is a growing exponential: $\delta c = \tilde{c} \exp(\alpha \xi)$, $\alpha \equiv -f'(0)/v_{\mathrm{f}} > 0$. As a result, the solution ahead of the front must be uniform. The only non trivial solution that may exist in this model is by assuming that at a given location, say at $\xi = 0$, $\partial_\xi u$ jumps to a value $(\partial_\xi u)_{\mathrm{f}} > (\partial_x u)_{\mathrm{c}}$, while c jumps to a value $c_* > c_-$. Provided $f(c) > 0$ for $c_* < c < 1$, equation (5) can be integrated from $\xi = 0$ to $\xi \to -\infty$ with the proper boundary conditions, ensuring the existence of a solution. Equation (6) then implies that:

$$\left(\frac{v_{\mathrm{f}}^2 - V^2(0)}{v_{\mathrm{f}}^2 - V^2(c_*)} \right) = \frac{(\partial_\xi u)_{\mathrm{f}}}{(\partial_\xi u)_0} > 1. \tag{7}$$

Because of our assumption that V^2 is a monotonously increasing function of c, $V^2(c_*) > V^2(0)$, equation (7) implies that v_{f}^2 must be larger than $V^2(c_*)$, hence, the wave is necessarily supersonic. The solution of this problem is not unique: assuming that c_* and $(\partial_x u)_{\mathrm{c}}$ are given, there exists a continuum of solutions parametrized by v_{f}, or equivalently, by $(\partial_\xi u)_{\mathrm{f}}$. The range of propagation velocity is: $V^2(c_*) < v_{\mathrm{f}}^2 < V^2(c_*) + (V^2(c_*) - V^2(0))(\partial_x u)_0 / ((\partial_x u)_{\mathrm{c}} - (\partial_x u)_0)$. In order that the stress remains finite everywhere (v_{f} is larger than the sound velocity in the stable phase), the value of the ratio $r_u \equiv (\partial_x u)_0 / (\partial_x u)_{\mathrm{c}}$ must be close to 1.

The fronts found in this problem are expected to be stable in the sense that a small amplitude perturbation added to the solution eventually decays, and a new stationary solution with possibly a slightly different velocity arises [19].

A better description of the front can be obtained by taking into account some loss term, such as diffusion. Below, we show that the degeneracy found above is lifted when $D \neq 0$.

In the $D \neq 0$ case, slow travelling waves can be obtained when the coupling between the phase transformation (the c-equation) and the stress does not turn on. This is effectively the case when the stress is always smaller than the threshold value, $(\partial_x u)_{\mathrm{c}}$. The problem reduces then to the standard reaction diffusion:

$$-v_{\mathrm{f}} \partial_\xi c = f(c) + D \partial_\xi^2 c \tag{8}$$

which is known to have solutions, propagating with a velocity $v_{\mathrm{f}} = \sqrt{DA/2}(c_+ - 2c_-)$ when $f(c) = Ac(c - c_-)(c_+ - c)$. The wave propagation is therefore controlled by diffusion. In the following, we consider the case where the sound velocity is much larger than the velocity of waves controlled by diffusion: $V(0)^2/(AD) \gg 1$.

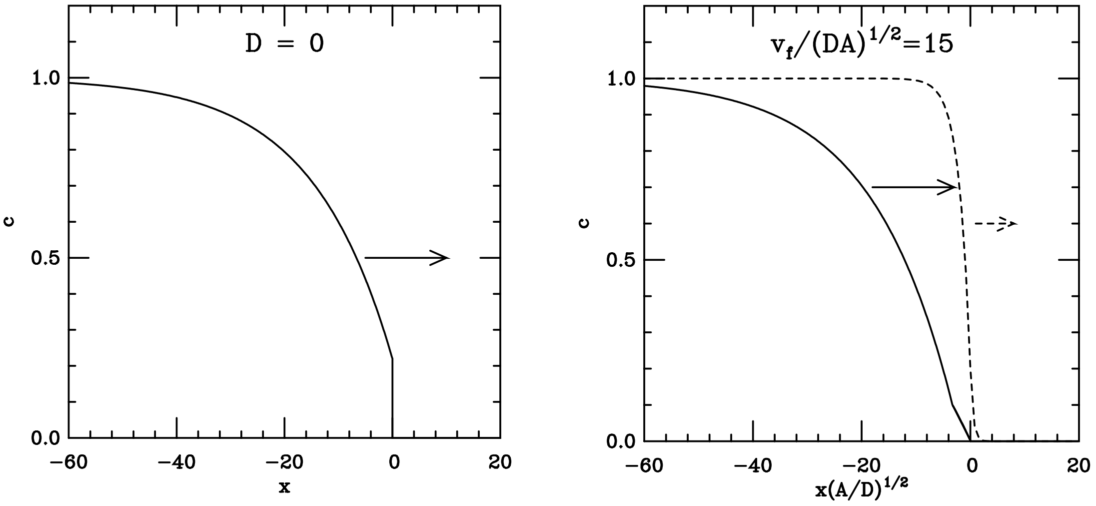
Once $c(\xi)$ is known, the stress $\partial_\xi u$ is determined from equation (6). The condition that the stress remains everywhere smaller than the threshold value is: $(\partial_x u)_0 (v_{\mathrm{f}}^2 - V^2(0))/(v_{\mathrm{f}}^2 - V^2(1)) < (\partial_x u)_{\mathrm{c}}$. Clearly, this condition is automatically satisfied if the velocity v_{f} is subsonic: $v_{\mathrm{f}} < V(0) < V(1)$, which is the case when D is small (we have assumed that $(\partial_x u)_0 < (\partial_x u)_{\mathrm{c}}$).

In addition to the family of slow propagating waves, driven by diffusion, and effectively without any coupling with the stress field, one may also find supersonic waves in this problem, provided the stress exceeds $(\partial_x u)_{\mathrm{c}}$. The value of c where the coupling term turns on, c_{s}, satisfies:

$$\frac{v_{\mathrm{f}}^2 - V^2(0)}{v_{\mathrm{f}}^2 - V^2(c_{\mathrm{s}})} (\partial_x u)_0 = (\partial_x u)_{\mathrm{c}}. \tag{9}$$

Once again, the wave must be supersonic ($v_{\mathrm{f}}^2 > V^2(c_{\mathrm{s}}) > V^2(0)$) for equation (9) to be satisfied.

The explicit determination of the solution of equation (5) requires a more complete calculation. The existence of a propagating solution can be proved provided the condition: $\int_0^{c_{\mathrm{f}}} f(c') \mathrm{d}c' + W_0 (c_{\mathrm{f}} - c_{\mathrm{s}}) > 0$, holds ($c_{\mathrm{f}}$ is the stable state under stress, solution of $f(c_{\mathrm{f}}) + W_0 = 0$). It can be carried out exactly in the simplified case where the function $f(c)$ is piecewise linear: $f(c) = -Ac$ if $c < c_-$ and $f(c) = -A(c_+ - c)$ otherwise, and with the extra assumption that the term $w(\partial_\xi u)$ never turns off, once it has been turned on, *i.e.*, $\tau \to \infty$. Anticipating that the physically relevant solution corresponds to a small value of the parameter c_{s} ($c_{\mathrm{s}} < c_-$), the solution may be determined by considering separately the three domains: (i) where $0 \leq c \leq c_{\mathrm{s}}$, (ii) where $c_{\mathrm{s}} \leq c \leq c_-$ and (iii) where $c \geq c_-$, by solving separately in each domain and then, by matching the solution and its derivative at the boundaries. In each domain, the solution can be expressed as a combination of exponentials: $c = A_- \exp(\alpha_- \xi) + A_+ \exp(\alpha_+ \xi)$, where $\alpha_\pm = (-v_{\mathrm{f}} \pm \sqrt{v_{\mathrm{f}}^2 + 4DA})/2D$, plus some constants, depending on the region (i–iii).



(a)

(b)

Fig. 2. Profile of the concentration c, when $D = 0$ (a) and when $D \neq 0$ (b). The profiles shown were obtained by solving the reaction diffusion equation with the piecewise linear function: $f(c) = -Ac$ when $c < c_-$ and $f(c) = -A(c_+ - c)$ otherwise (the parameters are $c_- = 0.2$, $c_+ = 1$). In (a), the size of the front is of order v_f/A; $c_* = 0.22$. In (b), the dashed line corresponds to the solution for the slow, diffusive wave ($v/\sqrt{AD} = 1.5$) and the solid line corresponds to the fast wave ($v_\mathrm{f}/\sqrt{AD} = 15$). The sizes of the fronts are of order v_f/A.

The matching condition leads to the relation:

$$c_\mathrm{s}\frac{(\alpha_+ - \alpha_-)}{\alpha_+} - \gamma = c_+ \exp\left[-\frac{\alpha_-}{\alpha_+}\ln\left(\frac{\alpha_- - \alpha_+}{\alpha_-}\frac{\gamma - c_-}{\gamma} - \frac{c_+}{\gamma}\frac{\alpha_+}{\alpha_-}\right)\right], \quad (10)$$

where $\gamma \equiv W_0/A$. As we are interested in velocities large compared to the diffusive velocity: $v_\mathrm{f} \gg \sqrt{DA}$, $\alpha_- \approx -v_\mathrm{f}/D$ and $\alpha_+ \approx A/v_\mathrm{f}$; hence $|\alpha_-| \gg |\alpha_+|$. In this limit, $(\alpha_- - \alpha_+)/\alpha_- \approx 1 + (AD)/v_\mathrm{f}^2$, so the RHS of equation (10) reduces to $c_+ \exp(v_\mathrm{f}^2/(AD)) \ln(1 - c_-/\gamma + \mathcal{O}(1/v_\mathrm{f}^2))$, a term that tends to zero when $v_\mathrm{f} \to \infty$. As the right hand side of equation (10) reduces to $\approx c_\mathrm{s} v_\mathrm{f}^2/(AD) - \gamma$, one finds that $c_\mathrm{s} \approx \gamma DA/v_\mathrm{f}^2$, or equivalently:

$$v_\mathrm{f} = \sqrt{\frac{DA\gamma}{c_\mathrm{s}}}\,. \quad (11)$$

Importantly, this value of v_f can be made arbitrarily large, by letting the value of c at the shock, c_s, go to 0. Mathematically, equation (11) expresses that the rapidly growing mode when $\xi \to -\infty$ must remain bounded behind the shock (for $\xi \lesssim 0$). For this reason, we expect that equation (11) is in fact independent of the precise shape of the function f. The concentration profile of the solution is shown in Figure 2. The profile of the fast wave (full line) is broader than the profile of the slower, diffusive wave (dashed line) by a factor $\approx v_\mathrm{f}/\sqrt{DA}$.

To completely determine the solution, one must solve simultaneously the two equations (9, 11), which leads to:

$$\frac{DA\gamma}{c_\mathrm{s}} = \frac{V^2(c_\mathrm{s})(\partial_x u)_\mathrm{c} - V^2(0)(\partial_x u)_0}{(\partial_x u)_\mathrm{c} - (\partial_x u)_0}\,. \quad (12)$$

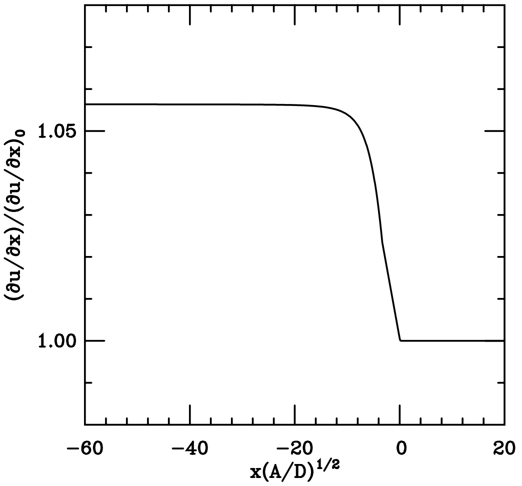


Fig. 3. Schematic profile of stress, $\partial_x u$ corresponding to the fast wave solution shown in Figure 2b. The velocity chosen is $V^2(c) = V^2(0)(1 + 0.2\tanh(x/0.2))$; $(\partial_x u)_\mathrm{c}/(\partial_x u)_0 = 1.04$.

Since $V^2(0)/AD \gg 1$, the solution of this equation is small: $c_\mathrm{s} < \gamma DA/V^2(0)$. The propagation velocity increases when the ratio $r_u \equiv (\partial_x u)_0/(\partial_x u)_\mathrm{c}$ increases, and diverges when $u \to 1$. In order to avoid the divergence of strain previously discussed, propagating waves may only exist when the ration r_u is close enough to 1, so the propagating velocity is larger than the sound velocity in the stable phase. The stress profile in the case $(r_u - 1) \ll 1$ is shown in Figure 3.

In conclusion, we have proposed a simplified model describing propagation of fast detonation like autowaves, resulting from an interaction between mechanical stress and phase or chemical transformation. Although our model is somewhat preliminary and calls for improvements, we expect that the physical ideas put forward are important to understand fast propagation in condensed phases.

We have shown the existence of two branches of propagating wave solutions of equations (1, 2) when $D \neq 0$. The slow, diffusive waves are obtained when the coupling between chemistry and mechanical stress does not turn on. They simply correspond to the well-known propagating fronts, familiar in the context of reaction diffusion systems. The fast, supersonic waves are obtained when the mechanical stress reaches the critical value, $(\partial_x u)_c$, so the coupling term w turns on and it starts the phase (chemical) transformation. Interestingly a continuum of fast (supersonic) solutions also exists when $D = 0$. The introduction of a diffusion term, effectively a loss term, selects out of this infinite set a unique wave. We suspect that the introduction of a loss term in the mechanical equation would lead to a qualitatively similar result. In this sense, the situation is very reminiscent of the situation in gaseous detonation. The presence of two branches of solutions has also been observed in the reaction-diffusion model proposed in [12,13] to describe the coupling between thermal stress and phase transformation. The model we have considered in this paper is mathematically very different since the problem is of hyperbolic type, which is natural to describe propagation of elastic waves. The results obtained in this work suggest a rich and interesting structure.

Our model may capture the fast (supersonic) waves found in heavy metal azides and in hard glasses, but most likely fail to describe the propagation regimes found in "detonation boiling" and cryochemistry, which are found to be subsonic. Stability issues have not been addressed in this work. We simply remark that fast solutions are very sensitive to perturbations of the stress field ahead of the front. Interesting questions concerning the time evolution of the solution, and the influence of the finite size of the samples (particularly important since the reaction front is found to be very wide) remain to be studied. The problem of propagation of a stable state into an unstable state ($f(c) = Ac(c_+ - c)$) leads to an interesting selection problem [2], which will be investigated separately.

It is a pleasure to acknowledge A.M. Stolin for useful discussions, and V.I. Krinsky for making this work possible, and for his constant interest and support.

References

1. M. Cross, P.C. Hohenberg, Rev. Mod. Phys. **65**, 851 (1993).
2. A.N. Kolmogorov, I. Petrovsky, N. Piskunov, Bull. Univ. Moscow, Ser. Int. Sec. A **1**, 1 (1937).
3. Ya.B. Zeldovich, G.I. Barenblatt, V.B. Librovich, G.M. Makhviladze, *The mathematical theory of combustion and explosion* (Consultants Bureau, 1985).
4. P. Clavin, Ann. Rev. Fluid Mech. **26**, 321 (1994).
5. L.D. Landau, E.M. Lifshitz, *Fluid Mechanics* (Pergamon Press, 1960).
6. J.D. Murray, *Mathematical biology* (Springer, New York, 1989).
7. V.A. Shklovskii, Zh. Eksp. i Teor. Fiz. **82**, 536 (1982).
8. C. Meade, R. Jeanloz, Nature **339**, 331 (1989).
9. J.S. Olcott, Science **140**, 1189 (1963).
10. T.V. Polyakova, I.M. Fomin, D.N. Karpinskii, Dokl. Akad. Nauk **311**, 431 (1993).
11. V.V. Barelko, S.M. Ryabykh, K.Sh. Karabukaev, Sov. J. Chem. Phys. **12**, 377 (1994).
12. V.V. Barelko, I.M. Barkalov, V.I. Goldanskii, D.P. Kiryukhin, A.M. Zanin, Adv. Chem. Phys. **74**, 339 (1988).
13. V.V. Barelko, I.M. Barkalov, V.I. Goldansky, A.M. Zanin, D.P. Kiryukhin, Russ. Chem. Rev. **59**, 205 (1990).
14. N.S. Enikolopyan, Dokl. Akad. Nauk SSSR **283**, 897 (1985).
15. S.A. Zhukov, V.V. Barelko, Int. J. Heat Mass Transf. **35**, 759 (1992).
16. L.Q. Chen, Y. Wang, A.G. Khachaturyan, Philos. Mag. Lett. **64**, 241 (1991).
17. S. Semenovskaya, A.G. Khachaturyan, Phys. Rev. Lett. **67**, 2223 (1991).
18. The results obtained here can be generalized in the case where $c = 0$ is an *unstable* equilibrium point, A. Pumir, V.V. Barelko (in preparation).
19. E.L. Pechatnikov, V.V. Barelko, Sov. J. Chem. Phys. **4**, 2092 (1987).